NICHROME RESISTOR PROPERTIES AND RELIABILITY

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NICHROME RESISTOR PROPERTIES AND RELIABILITY

Clyde H. Lane

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A collection of the physical properties of nichrome films is given in this report. Graphs are presented giving property variations as functions of composition, deposition rate, method of deposition, substrate morphology etc. Failure mechanisms such as electromigration interdiffusion, corrosion and electrocorrosion are addressed and specific information is given with regard to real, possible and unlikely mechanisms. The report is intended to give a composite review of nichrome resistor technology from a process and

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20. reliability point of view.

NICHROME RESISTOR PROPERTIES AND RELIABILITY

Clyde H. Lane

PREFACE

This report is a compilation of the work of many people. Contributors at RADC include Captain Raymond Bellem, Vincent Kapfer, John Bart, Robert Thomas and Benjamin Moore. The author thanks these people and other members of the Reliability Branch, RADC, for test pattern fabrication, report preparation and editing.

This report, prepared by Clyde H. Lane, under Job Order No. 55190447, has been reviewed by the Office of Information (OI), RADC, and approved for release to the National Technical Information Service (NTIS).

This report has been reviewed and is approved.

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ABSTRACT

A collection of the physical properties of nichrome films is given in this report. Graphs are presented giving property variations as functions of composition, deposition rate, method of deposition, substrate morphology etc. Failure mechanisms such as electromigration interdiffusion, corrosion and electrocorrosion are addressed and specific information is given with regard to real, possible and unlikely mechanisms. The report is intended to give a composite review of nichrome resistor technology from a process and reliability point of view.

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NICHROME RESISTOR PROPERTIES AND RELIABILITY

INTRODUCTION:

Nichrome thin film resistors have been used in microcircuit fabrication since about 1960. Several reliability studies were conducted and the system generally received a clean bill of health. Use of nichrome film resistors on silicon integrated circuits was initiated to improve circuit performance. In this technology, resistor widths were reduced from about 0.010 to 0.001 inches or less and oxidized silicon became the substrate. At this time, RADC began to be concerned about long time effects. An in-house program was started and we began to query users and vendors about possible nichrome problems. Following evidence from our in-house study and some information from a user concerning a nichrome problem, a contract was initiated to study the situation. Because of rapid developments in the area of nichrome resistor failures prior to letting a contract, a good deal of in-house information was accumulated. In this report, a summary of nichrome resistor technology is provided as well as the results from our own investigations.

RADC NICHROME INVESTIGATIONS

The first reliability physics studies of thin film nichrome resistors in the Air Force were done under RADC contracts and are documented in RADC-TR-65-287, RADC-TR-65-514 and RADC-TR-66-495. At this time we looked for intermetallic formation, aging mechanisms in the films, and the influence of a passivating layer. A direct etch technique for fabricating nichrome films was developed in-house, so that possible reliability problems with the new variations in nichrome resistor technology could be investigated.

A special resistor test pattern was made to allow studies of line definition, contact resistance, and lifetime under varying conditions of voltage, current density and passivation. The process established was as follows:

1. Evaporate nichrome from a tungsten boat using a fresh boat and material each time. Sheet resistance is controlled by a monitor slide.

2. Evaporate aluminum over the nichrome in the same pump down vacuum 1×10^{-5} to 1×10^{-6} Torr.

3. Etch aluminum - define contact pads.

4. Etch nichrome - define resistors.

5. Stablize the resistors - 400° for 30 min.

6. Overcoat with protective material if desired.

On 11 Sept 1970, 60 resistors fabricated in this way were put on life test. The test was terminated on 28 Jan 1971. Seven resistors failed catastrophically during the first measurement period, (one month); after that the resistors changed less than 1%. The test had been set up so that about half the devices had one volt applied bias while the other half had 10 volts applied. The current was adjusted to maintain equal power densities in resistors with the different voltages. Half of each group had a passivating film of hardened photoresist while the other halves had no passivating layer. The test was run under room conditions, only a dust cover was provided by placing the devices on TO_5 headers and placing the tops on, but not sealing them.

Only devices having the 10 volt applied bias failed and six of the seven failed resistors had no passivating layer. In the one device which did have passivation, a break in that film, clearly associated with the opened resistor, was seen under microscopic investigation. These results

led us to conclude that electrochemical corrosion was the cause of failures. The corrosion cell required more than one volt potential to initiate the reaction. This sounded very much like we were dealing with a reaction which required the dissociation of water. To test this idea, two nichrome films were placed into a beaker of distilled water so that the water came about half way up the resistor. Bias was then applied and raised until a reaction occurred. That reaction was a bubbling of gas at the negative electrode and corrosion of the resistor at the positive side. When this experiment was run with 80NI-20Cr nichrome wire, the wire on the negative side stayed shiny while the wire on the positive side turned black and corroded away. Initially the solution turned yellow, but remained clear. As the reaction proceeded, however, the solution became cloudy and finally, a yellowish orange gelatinous precipitate formed. Our analysis of the reaction was that hydrogen was evolved at the negative electrode, while oxygen generated at the positive electrode immediately oxidized the nichrome, giving the black color. The oxide then formed the hydroxide, freeing nickel and chromium ions until the solubility limit of chromium hydroxide was reached, at which time it precipitated, forming the gelatinous material. Additional tests with water drops on film resistors confirmed that a certain potential was necessary for the reaction to occur and the film opened on the positive side. The potential was, approximately, the potential necessary to dissociate water on the nichrome. Reaction times varied slightly for different substrates and it was assumed that contaminants varied the conductivity of the water and affected reaction times in that way.

The conclusion that the nichrome problem some people were experiencing, was really electrochemical corrosion, was slow in forming. At first, the

problem seemed to be electrical overstress, poor contact with aluminum, intermetallic formations, or electromigration. During discussions with industry representatives and particularly with investigators at Crane Naval Ammunition Depot, the problem was shown to be lot sensitive and to affect every manufacturer. Corrosion was discussed only briefly. Additional consideration of our data, and information from industry and the Navy, relative to low temperature burn-in as a screen, firmed up the hypothesis of electrochemical nichrome resistor attack, as a result of water vapor condensed in glassivation cracks or voids. The water vapor came from devitrification of glass used in sealing the package. Variations in the glass and glass application process were responsible for the lot sensitivity. A discussion of room and below-room temperature burn-in failures, water drop test, cracks in SiO, condensation experiments, and outgassing of package materials was provided by industry and the Navy. On 2 July 1971, a report from an industrial source was sent to RADC which discussed corrosion of nichrome in a high humidity atmosphere. The report stated that high humidity and high current would cause accelerated resistor material corrosion. It was reported to the author[1] however, that nichrome films will not fail under pure, deionized water if the substrate is ion free and a blanket of inert, contamination-free gas is kept over the test. It was also noted[2] that under clean conditions an applied voltage of 1.4 volts was necessary before corrosion could occur. Certain contaminants can apparently lower this value since we found that corrosion took place down to about one volt in tap water.

An RADC investigation of the reliability of radiation hardened quad Nand gates[3] shed some light on nichrome resistor reliability. These low

power, radiation hardened gates, had a large portion of the chip real estate dedicated to nichrome resistors. Elevated temperature testing produced no nichrome failures. One hundred circuits were tested. But, when ten circuits were placed on a cycled low temperature test under bias, two nichrome failures were recorded at -23°C. In the next test, 80 circuits not previously tested, were held at 125°C for 5 hours. The circuits were then brought to room temperature and placed on a low temperature cycle test; +25°C to -10°C and back to 25°C over a 24 hour period. Power was cycled on and off during the test. Sixteen nichrome resistor failures occurred. Mass spectrometer analysis of the internal environments of the packages showed a definite correlation between failed devices and water content in the packages. Table I gives that important information.

TABLE I

Correlation of Water Vapor With Failed Circuits

	AVE. VALUE of H_2O In The Package	STD. DEV.
Stressed & Failed	1.7%	0.9
Stressed, No Failures	0.72%	
Unstressed	0.22%	

The mass spectrograph information leads one to suspect continued outgassing of water vapor during the 125°C bake. This water condensed during the low temperature cycle and caused the failures by electrochemical corrosion. Because the circuits were glassivated, i.e., the entire chip, with the exception of the bonding pads, was covered with an evaporated SiO_2 film, the moisture could only access the resistors through cracks or holes in that glassivation. During our earlier work in-house, it was realized that a

crack or pin hole is a preferred site for condensation because the vapor pressure of water in a capillary is less than the vapor pressure of water on a flat surface. Thus, one has thephenomenon of capillary condensation which is very detrimental in this situation. One can make a good case for the fact that a crack must have a minimum width depending on applied voltage,or else the crack must extend across two conductor paths in order to achieve the required voltage to turn on the electrochemical corrosion cell.

Straightforward chemical corrosion can occur as long as the appropriate ions are present. The crack or pin hole simply provides access to the nichrome. Evidence of simple chemical corrosion on the quad gates was later found also. This fact implicates process control in resistor fabrication as well as in packaging. The Scanning Electron Microscope (SEM) photograph in Figure 1 shows another process control problem, poor step coverage of the aluminum-nichrome termination by the evaporated glass. This forms a pocket which readily catches available water.

Unsatisfactory Glass Coverage of the Aluminum Contact to a Nichrome Resistor

Figure 1

An investigation of the electrical overstress resistance on the 350 ohm output resistor of the quad gates previously mentioned[3] showed that the average power in watts required to destroy the 150 ohm per square material (approximately 60% nickel - 40% chromium) was 111 ± 10%. A one microsecond pulse was used. The average was taken from ten values.

This essentially completed the in-house work except for that undertaken in direct support of the contract. Other in-house work which bore on the problem was that related to microcrack generation in silicon dioxide passivation and various deposited glassivation films[4]. In that referenced technical report entitled, "Reliability Problems with SiO_2 Passivation and Glassivation", the ease with which certain glass and SiO_2 films could be cracked due to thermal differential expansion and contraction between the glass and the aluminum metallization was demonstrated.

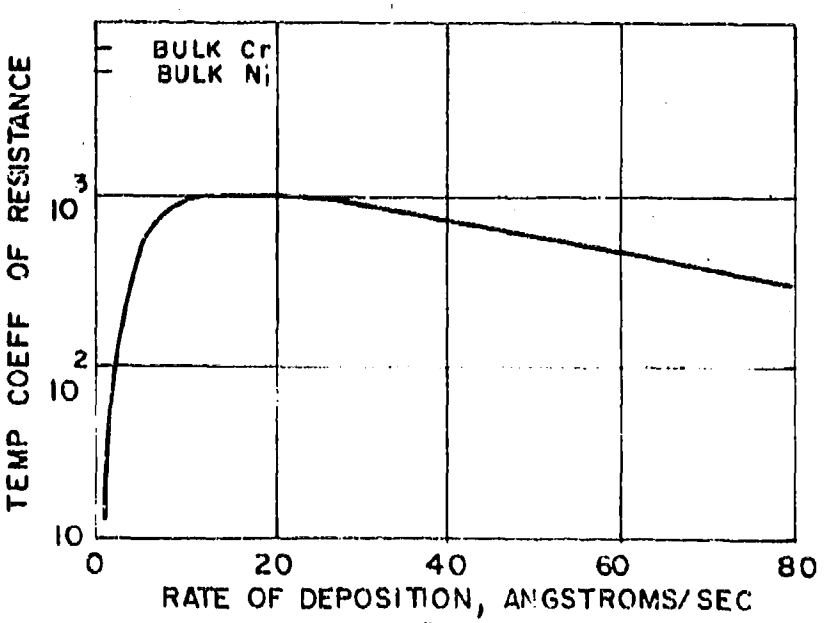
LITERATURE SURVEY

Unfortunately, there is little in the literature which applies directly to the problem at hand (i.e., the reliability of nichrome film resistors on thermally oxidized silicon substrates). One may find a host of papers which deal with the properties of bulk nichrome and associated alloys. A selected bibliography is provided by references 5-14. Evaporated nichrome films for resistors are generally between 50 and 200 angstroms thick. Their behavior and properties cannot be satisfactorily estimated from bulk materials. Film behavior is dominated by thickness, substrate material, surface conditions, vacuum conditions and exact evaporation or sputtering procedures. Most film resistor work reported, deals with evaporated 80Ni-20Cr alloy. Substrates were crown or pyrex glasses or glazed alumina. Tungsten boats or filaments were generally used as resistance heated sources. Resistors were 5 to 50

mils (.001 inches = 1 mil) wide. Resistor delineation was accomplished by evaporation through a metal mask held tightly to the substrate. Although nichrome films on thermal silicon oxide may differ as to the problems encountered, their properties are similar to these earlier evaporated films. Thus, some of these properties will be discussed.

Figure 2 presents a graph of the Temperature Coefficient of Resistance (TCR) for 100-150 ohm per square nichrome films, evaporated from an 80Ni-20Cr source at 5 X 10^{-4} Torr, as a function of the deposition rate. Also plotted are the TCR's for bulk nickel and chromium. This information comes from a paper by Siddall and Probyn[15]. Notice that the film has a lower TCR than the bulk constituents for all deposition rates. Also notice that low deposition rates give low TCR's.

Temperature Coefficient of Resistance
for 100-150 Ohms/Square Nichrome Films
Evaporated from an 80NI:-20CR Source
at 5X10^{-4} Torr
Figure 2



This is due to the incorporation of oxides of nickel and chromium. When the composition becomes one of nichrome particles dispersed in a dielectric medium, the TCR will become negative. The variation of TCR with deposition rate reflects a Ni/Cr ratio change in the film as well as different oxide content. Chromium sublimes at a lower temperature than nickel melts. Lower evaporation rates favor increased chromium content. If the same source is used over and over, the relative amount of chromium will become depleted giving higher nickel contents for the same rate. This fact was shown by Lakshmanan[16]. The TCR variation with number of depositions from the same scurce is best shown in a publication by Taylor[17]. Since the exact graph depends on the exact system and materials used, it is sufficient to indicate that the TCR became increasingly positive with succeeding depositions. In the early depositions the chromium content is high. It falls with succeeding depositions. The TCR behavior is a good indication that the more reactive chromium is rapidly oxidized, and actually, to a large extent, is contained in the film as an oxide. Double oxides of nickel and chromium with a spinel structure have been detected by electron diffraction. According to Dushman[18] the structure of nichrome films is a dispersion of $Ni_{0.7}$ $Cr_{o.3}$ in a matrix of Cr_xO_y. For this reason the pressure, composition of the residual atmosphere, and the rate of deposition have a tremendous effect on TCR. Empirically, TCR has been correlated with:

(1) Very thin films

(2) Low deposition rates

(3) Large Cr/Ni ratios.

For these reasons TCR is a good measurement for process control purposes and can be a good indication of structure.

An RADC contractual study published in November 1964[19] noted the following structure; for a composition of 75% Ni, 20% Cr, 2.5% Al and 2.5% Cu, evaporated onto an alumina substrate, Table II:

TABLE II

Relationship of Nichrome Film Structure to Heat Treatment in Vacuum

FILM THICKNESS	HEAT TREATMENT (VACUUM)	STRUCTURE
300A	as deposited	Single phase poly-crystalline film
300A	350°C - 2 hrs.	Same as above, plus Ni_3Al precipitate
760A	350°C - 2 hrs. 575°C - 1 hr.	Ni_3Al precipitates have become larger and much further apart.

Oxidation of these films at from 250-350°C seemed to create a Cr_2O_3 surface film. Cr_2O_3 tends to be an electron excess semiconductor[20]. At film thicknesses of from 50 to 60 angstroms (sheet resistivity of approximately 300 ohms per square) the surface states of the Cr_2O_3 phase predominate, and stable films are possible only if encapsulated and prevented from further reaction with all environmental gases, especially hydrogen, oxygen and water vapor[21].

The 80%Ni-20%Cr alloy is a single phase. If sufficiently chromium enriched however, during evaporation, a second phase (chromium solid solution) precipitates.

Oxidation of nichrome films often occurs from nucleation centers, causing an uneven reduction of film thickness.

As previously stated, nichrome film properties are critically dependent on the exact materials, processes and process controls used. Pratt and McCarthy,[22] in an early paper on nichrome resistors offered the

following list, Table III, of variables to be controlled:

Variables to Control in Nichrome Deposition

TABLE III

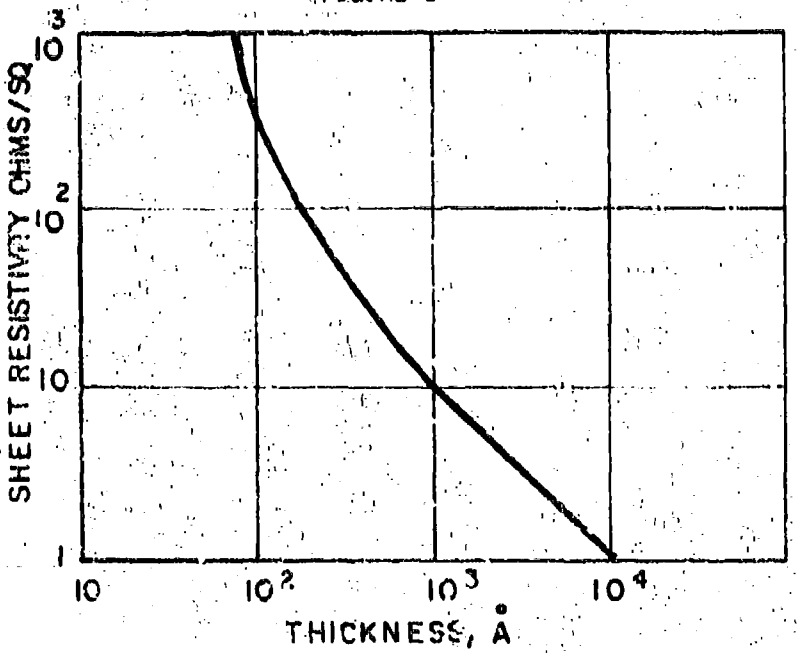
Composition	Ni/Cr Ratio Oxide Content Other Contaminants
Structure	Deposition Rate Deposition Time Source Temperature Pressure Uniformity Continuity Crystallographic Structure
Substrate	Surface Texture Temperature Cleanliness Expansion Coefficient

As one can readily see, these variables are not all independent.

Degenhart and Pratt[23] published a number of graphs on nichrome film properties. These graphs are reproduced as Figures 3,4,5 and 6. Figure 3 gives the variation in sheet resistivity with film thickness for boat or filament evaporation of an 80%Ni-20%Cr source onto glass substrates. Figure 4 gives the bulk resistivity variation with film thickness. It also contains a resistivity reference of 108 micro-ohm centimeters for the bulk 80%Ni-20Cr alloy. Figure 5 gives the TCR variation of these films with thickness, while Figure 6 provides an idea of how the sheet resistivity varies with the weight percent of nickel in the final film. The authors concluded from their studies that: 1. Starting at about 700 angstroms, the sheet resistivity of nichrome films evaporated from an 80Ni-20Cr source, deviates increasingly from the value expected from the bulk resistivity. 2. Fractionation and oxidation of the 80Ni-20Cr alloy takes place during

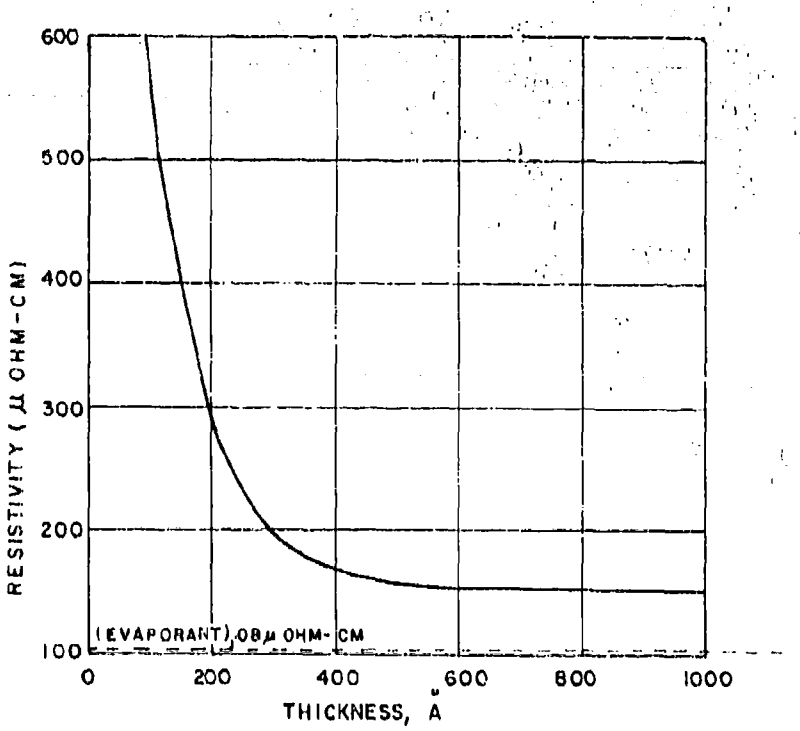
Sheet Resistivity vs Thickness For Evaporated 80Ni-20Cr Films on Glass Substrates

FIGURE 3

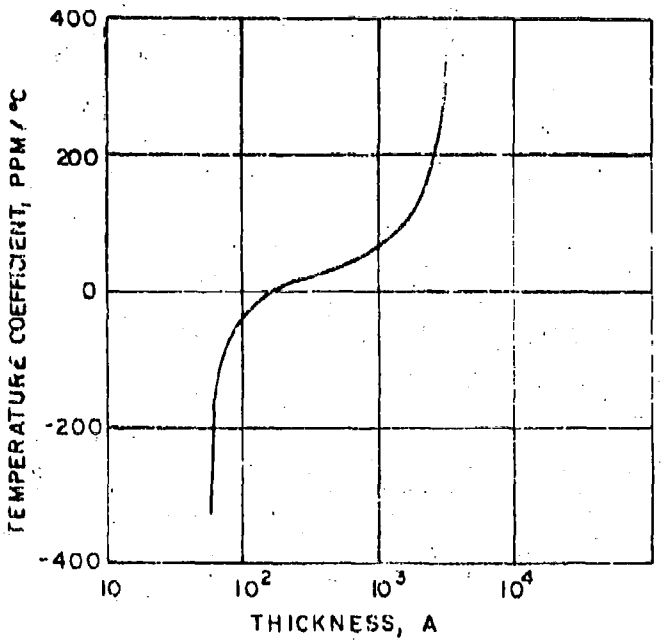


Resistivity vs Thickness for Evaporated 80Ni-20Cr Films on Glass Substrates

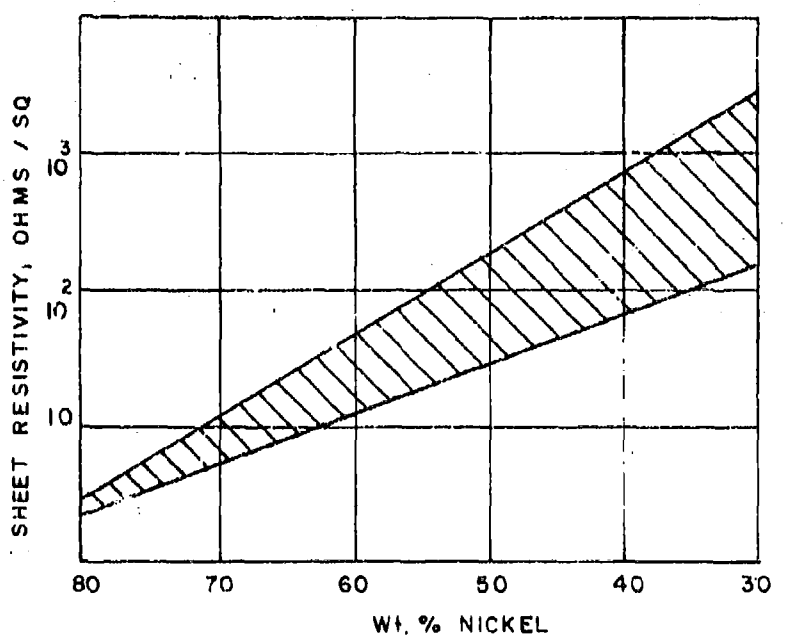
Figure 4



Temperature Coefficient of Resistivity vs Thickness of Evaporated 80Ni-20Cr Films on Glass Substrates
Figure 5



Relationship Between the Ni/Cr Ratio and the Sheet Resistivity in Films Evaporated From an 80Ni-20Cr Source Onto Glass Substrates
Figure 6



the evaporation and deposition processes. These effects, to a large measure, determine the sheet resistance and temperature coefficient of nichrome film resistors.

In October 1966, another final RADC contractual report[24] provided interesting information on nichrome film resistor characteristics and some insight concerning failure probability. Pertinent information, graphs, discussion and conclusions from that report follow.

FAILURE PROBABILITY VERSUS EFFECTIVE TEMPERATURE

It has been accepted for some time that thin film nichrome resistor reliability depends on the power being dissipated by the resistor. A simple expression to estimate effective film temperature is $T_{eff} = T_A + CP$ where

T_A = ambient temperature in °C

C = constant, °C/watt

P = power in watts

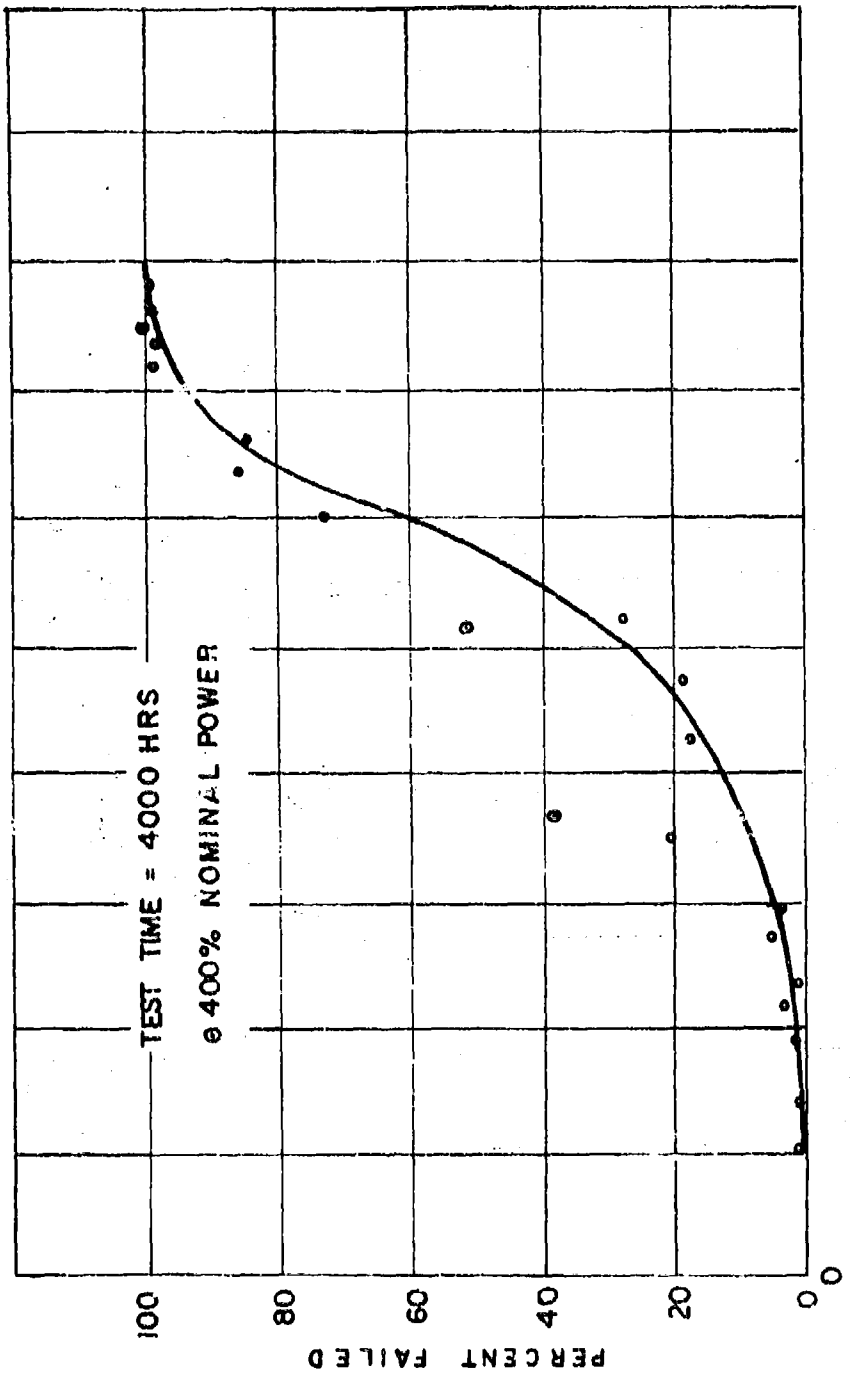
From a previous RADC technical report[19] we have a curve relating percent failure of a matrix of film resistors to the effective temperature. This graph is shown in Figure 7. For very high power dissipation, 400% of nominal, the relationship, valid at lower power dissipation, did not hold. The exact relationship depends on the exact system. It is obviously different for 60Ni-40Cr films on alumina, as opposed to 30Ni-70Cr films on one micron of SiO_2 thermally grown on silicon, and the whole composite protected by 2-3 microns of glass.

RESISTIVITY

Various compositions of nichrome have been used for thin film resistors. Figure 8 gives two plots of nichrome resistivity versus composition. The

Percent Failure as a Function of Teff

Figure 7



graph for bulk alloys was drawn using data from two references [25][26], one for the end points and the other for the portion shown as a solid line. The data for the thin film alloys is a composite of two sets of data from reference 24. No end points are available since we do not have a reference for the resistivity of 100 angstroms of chromium or nickel. The thinness of the films, the effect of contamination and the proportionately larger effect of any oxide surface or grain boundary oxidation on these very thin films should raise the terminal values of the curve substantially. Also in this figure, one sees the effect of tungsten contamination from the filament. The percent of tungsten varied in the films from 0 to 2.8 weight percent.

DENSITY

Density variation of nichrome alloys is of some interest, but the data for thin films shows a great deal of scatter. Nevertheless from Figure 9 it is evident that a maximum density of about 11 grams per cubic centimeter is reached at about 37 wt% chromium. The data is plotted from two sets of data in Reference 24. Liberty was taken to position the maximum where the maximum occurs in the resistivity versus composition curve. Also, end points were used and assumed to be the same as bulk values.

COMPOSITION VARIATION

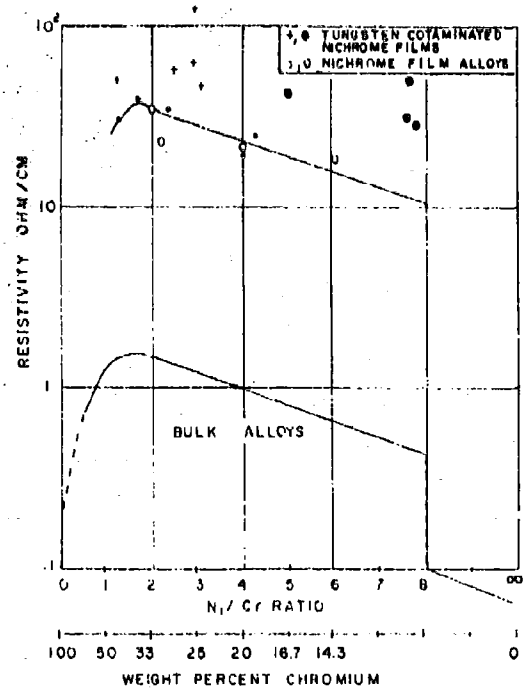
Using the "large melt" method of deposition, the percentage of nickel varied from 95 to 50% for a source composition of 80%Ni-20%Cr. Layers nearest the substrate had the highest chromium concentration[19]. More uniform films are obtained by flash evaporation, i.e., dropping powdered material onto a hot plate such that evaporation is almost instantaneous.

AGING CHARACTERISTICS

The most striking behavior of evaporated nichrome films was the fact

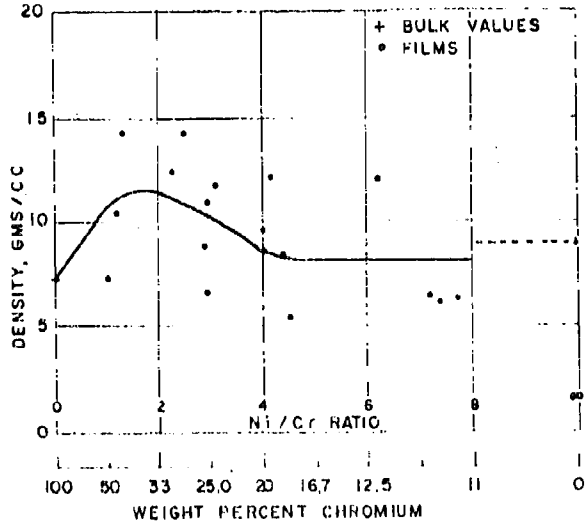
Resistivity versus Composition for Nichrome Alloys.

Figure 8



Density versus Nichrome Composition

Figure 9



that the filament evaporated films showed a rapid increase in resistance which then leveled off at a change increment which depended on the temperature, while the flash evaporated films showed a rapid decrease in resistance which leveled off and then started to increase. The greater the temperature, the greater the resistance change before leveling off. Figure 10 shows aging characteristics for source compositions of 80Ni-20Cr and 40Ni-60Cr. From this graph it does not appear that alloy composition has a large effect on aging characteristics. Another set of aging experiments on 7059 glass does not show the separation based on filament or flash evaporation. Neither do they show a consistent composition dependence. But as Figure 11 clearly shows, stability was achieved with a smaller change in resistance when power was applied during aging. A paper by Laski and Roth[27] showed a strong correlation between aging behavior and surface roughness. On the rough substrates film resistance increased rapidly. This was probably due to oxidation, which had a more pronounced effect on the resistors deposited on the rougher alumina surfaces, than on the smooth glass surfaces.

EFFECT OF SUBSTRATE AND CONTACTS

Resistor deterioration was pronounced for nichrome films on soda lime glass after 4 days in an oven at 100°C. 40 volts were applied to the resistors. Similar resistors on quartz treated the same way showed no sign of deterioration. Sodium migration from the glass is indicated as a strong factor in this deterioration but the exact mechanism was never worked out.

STRESS IN NICHROME FILMS

Nichrome has a bulk expansion coefficient of 1 .7 X 10^{-5}/°C

Soda-Lime Glass-9 .2 X 10^{-6}/°C

Borosilicate -(7059) 3 .6 X 10^{-6}/°C

Quartz - 0 .6 X 10^{-6}/°C

FIGURE 10

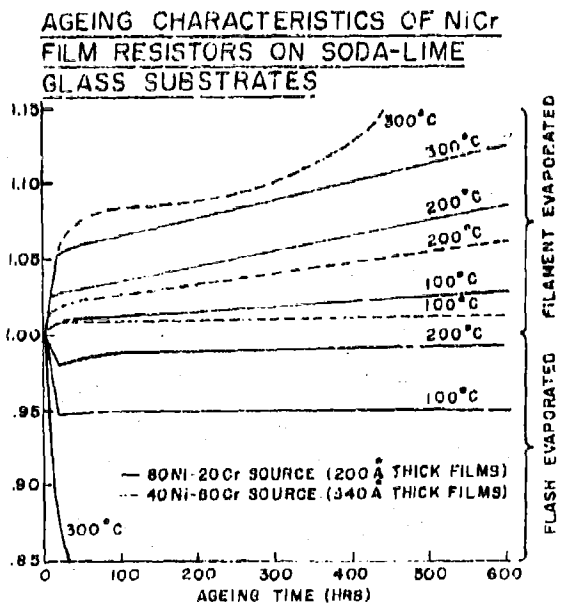
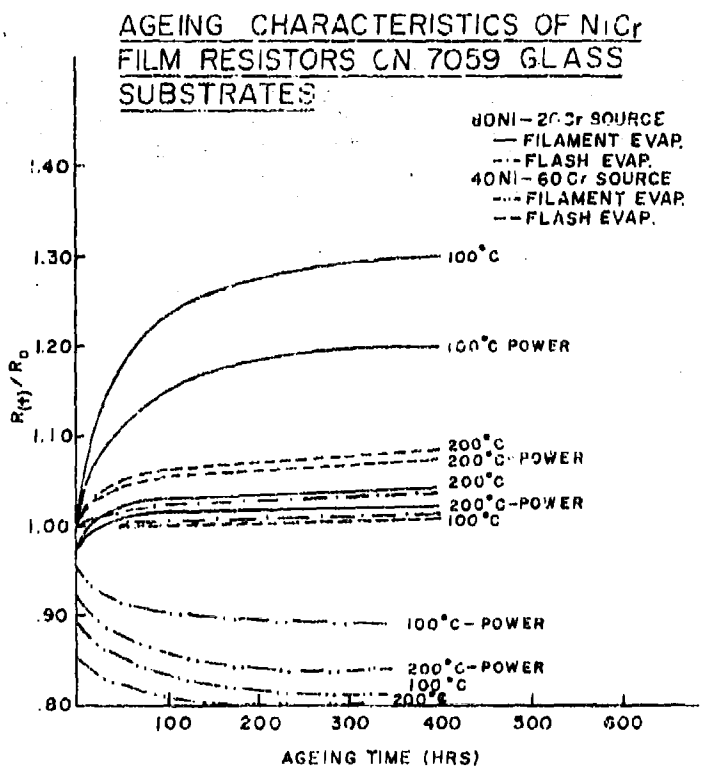


FIGURE 11

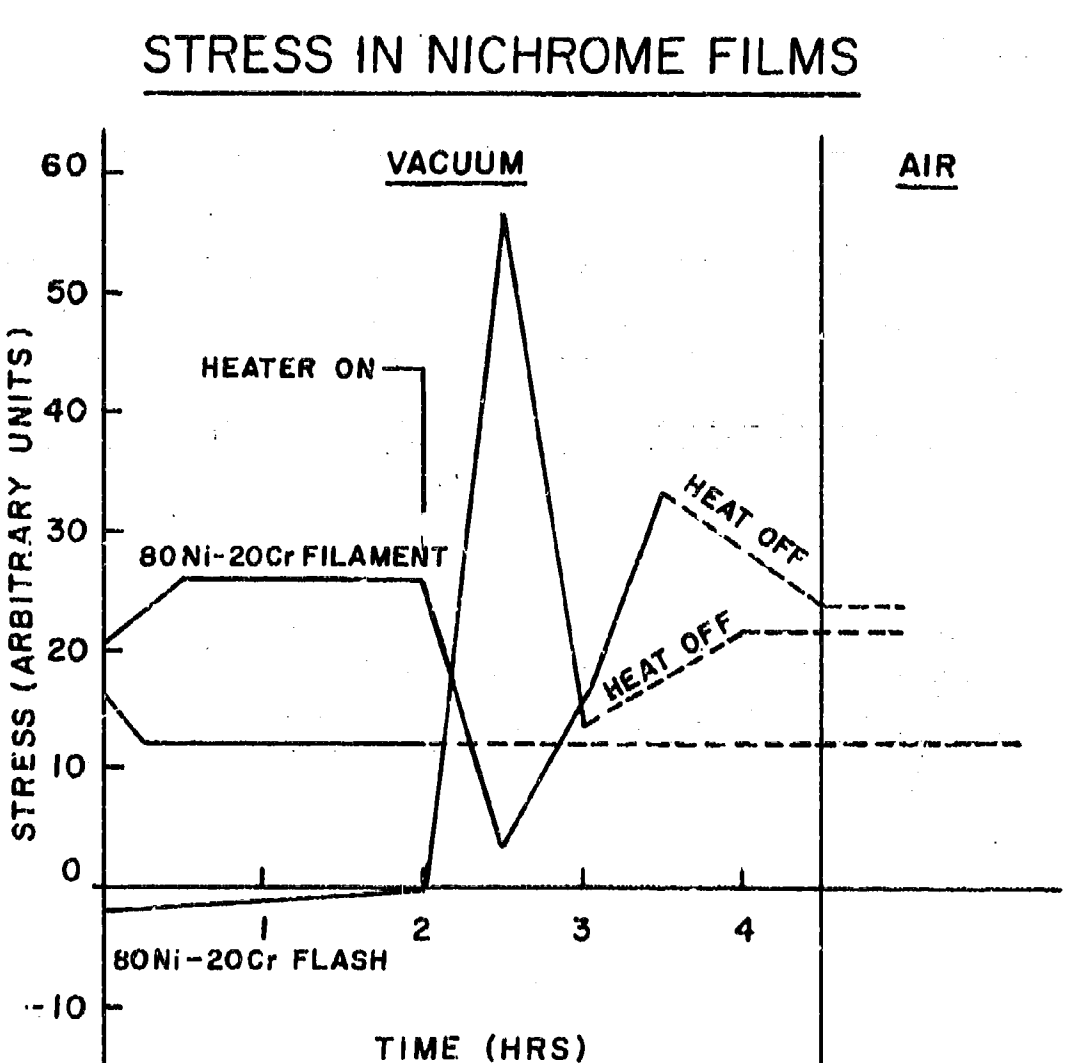


At the instant of deposition the filament evaporated film had a high tensile stress, while the flash evaporated film was in slight compression. Upon cooling the filament evaporated film changed slightly; the flash evaporated films did not change. Upon subsequent heating via infrared lamps and cooling to room temperature, both types of films stabilized at a moderate tensile stress. The measurements were made in vacuum, but virtually no change was seen upon exposure to air. This information is plotted in Figure 12. The most stable films are deposited at substrate temperatures between 250 and 350°C. Sheet resistivities should be kept below 200 ohms per square. Recently, a paper by Rairden, Neugebauer and Sigsbee[28] suggests that a barrier layer between nichrome and gold would be advisable where gold contacts are used. This is because the resistance of gold on chromium metallization will increase and then decrease during heating because of interdiffusion. The activation energy for the process is about 1.1 ev. If held at 400°C, the maximum resistance is reached in about 2 hours for quartz or oxidized silicon substrates, and about 0.2 hours for glass substrates. After 100 hrs at 400°C the chromium will have been completely transported through the gold film. Adherence to the quartz or thermally grown SiO_2 will have been completely destroyed. The chromium is removed by oxidation at the surface.

The same mechanism holds for Ni-Au couples, but the rate of resistance change is lower.

An early study by Lessor, Skerritt, Thun and Weed[29] revealed the susceptibility of nichrome to electrochemical corrosion. The purpose of the test was to evaluate in an accelerated manner, the effects of high

FIGURE 12


STRESS IN NICHROME FILMS
VACUUM
AIR
60
50
40
30
20
10
0
-10
STRESS (ARBITRARY UNITS)
HEATER ON
80Ni-20Cr FILAMENT
HEAT OFF
HEAT OFF
80Ni-20Cr FLASH
1
2
3
4
TIME (HRS)

humidity - high temperature on components containing nichrome resistors. Method 106, Moisture Resistance, of MIL-STD-202 was used. On 12 Sep 63, this became MIL-STD-202C. The same method was included in MIL-STD-883 as Method 1004, Moisture Resistance. This test differs from the steady state humidity test and derives its added effectiveness from the employment of temperature cycling, which provides alternate periods of condensation and drying, essential to the development of some corrosion processes. In addition, it produces a "breathing" action of moisture into partially sealed containers. The test includes low temperature and vibration sub-cycles that act as accelerants, to reveal otherwise indiscernible evidences of deterioration. Stresses caused by freezing moisture and accentuated by vibration tend to widen cracks and fissures. As a result, the deterioration can be detected by measurement of electrical characteristics, such as dielectric withstanding voltage and insulation resistance. Provision is made for the application of a polarizing voltage across insulation to investigate the possibility of electrolysis which can promote eventual dielectric breakdown. The test also provides for electrical loading of certain components, if desired, in order to determine the resistance of current carrying components, especially fine wires and contacts, to electrochemical corrosion. This test has proved reliable for indicating those parts which are unsuited for tropical field use.

The procedure used was as follows:

(1) Submit to ten continuous cycles as specified

a. Dry 24 hrs. 50°C, no humidity control

b. Drop to room temperature, take initial measurements

c. Up to 65°C, relative humidity (R.H.) 90-98%, 5 hrs.

e. Up to 65°C-R.H. 90-98%, 5 hrs.

f. Down to room temperature, R.H. 90-98%, X hrs.

g. Drop to - 10°C, 3 hrs, R.H. uncontrolled

h. Up to room temperature.

i. Vibrate 15 min., stay Y hrs.

Optional Step

X = not less than 1 nor more than four hours

Y = sufficient to complete 24 hours

POLARIZATION AND LOAD

When applicable, polarization voltage shall be 100 volts or as specified. The loading voltage shall be as specified.

FINAL MEASUREMENTS

Room temperature, following conditioning at 50% uncontrolled R.H.- 24 hours.

Figures 13 and 14 give the results of the tests. Figure 13 gives assurance that the resistors were good under elevated temperature conditions. Figure 14 shows that all resistors on test failed the temperature-humidity-power test catastrophically at 800 hours.

To the author's knowledge, this 1962-63 study is the only early indication of an electrochemical corrosion problem with nichrome films.

Information on electrochemical corrosion of nichrome films was provided to us by an industrial laboratory[30]. In one test, constant currents were passed through six, 20,000 ohm resistors held at 70°C. Two were operated at 5 ma, 2 at 2.5 ma and 2 at 1.5 ma. The time to failure as a function of current is shown in Figure 15. These resistors were potted in black epoxy. Also shown in Figure 15 are results from 6 similar resistors baked in

Figure 13
Component Reliability Nichrome Resistors 200°C Storage

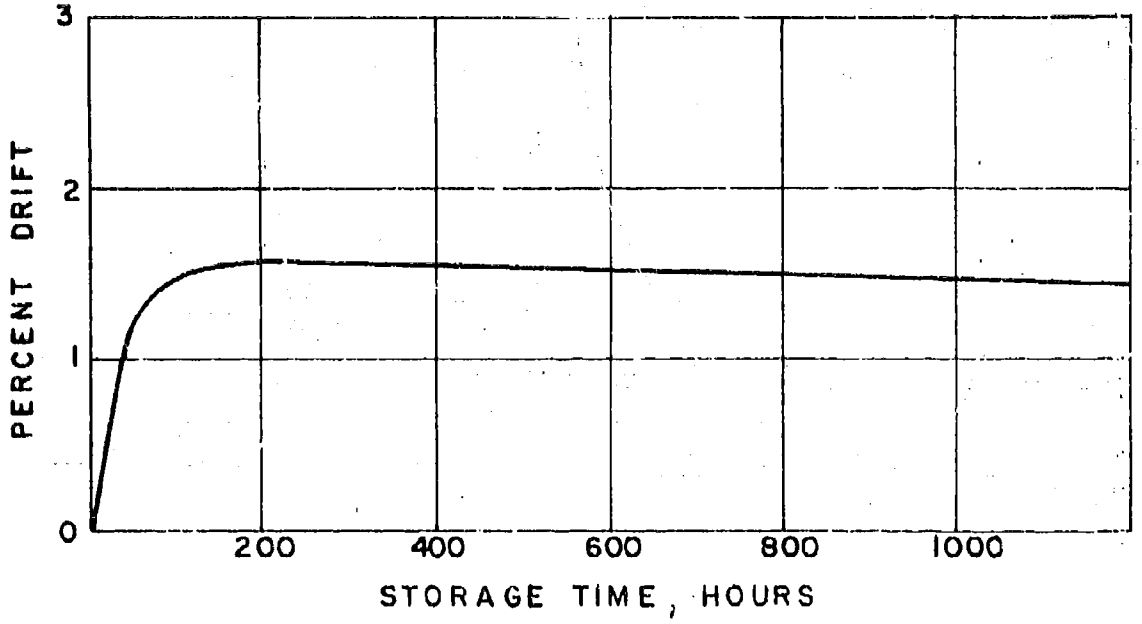
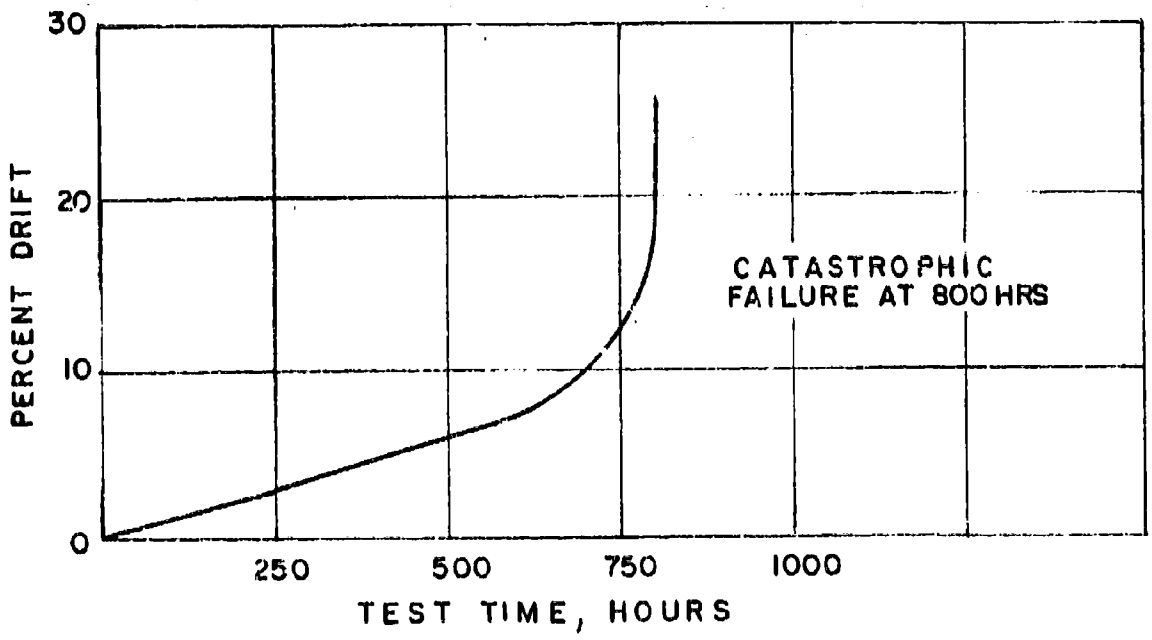
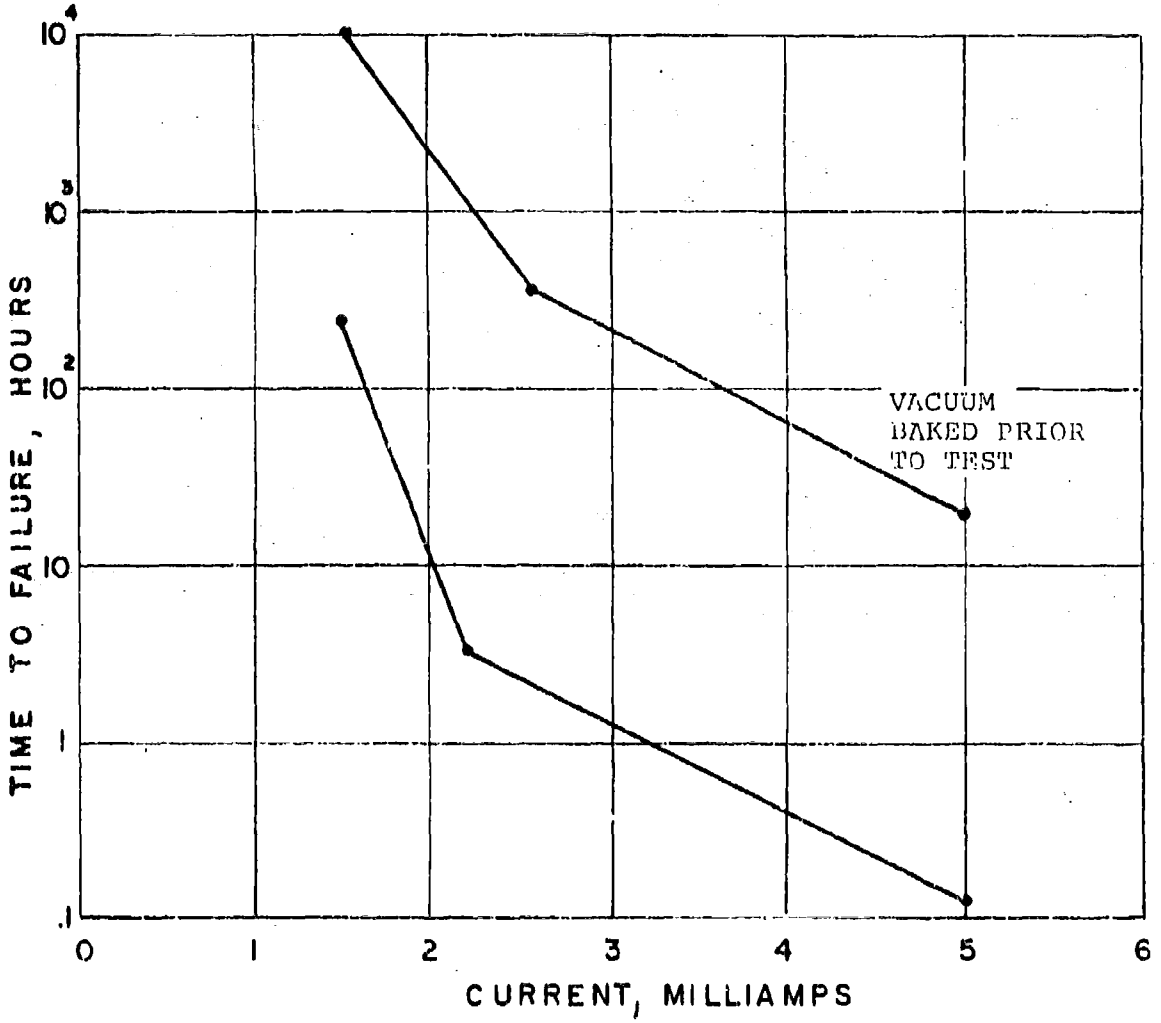


Figure 14
Nichrome Resistors-Temperature Humidity-Power
Testing- MIL-STD-202, Method 106A Power From 0-11 W/IN^2



Time to Failure as a Function of
Current for 12, 20K Ohm Resistors

Figure 15



vacuum at 100°C for 65 hours prior to testing at 70°C in a normal humidity environment. Obviously, increased current accelerates the failures and vacuum baking retards the time to failure. Another test on 80 hybrid circuits employing thin film nichrome resistors was conducted in accordance with MIL-E-5272C (ASC) Humidity Test. The procedure was:

1. Raise temperature from 25°C to 71°C over 2 hour period.
2. Hold at 71°C for 6 hours.
3. Drop temperature from 71°C to 25°C over 16 hours.
4. Maintain a constant relative humidity of 95% throughout the test.

Three resistors were powered on each circuit; one at 5 ma, one at 2.5 ma and one at 1.5 ma constant current. Many different packaging schemes were tested, but several observations pertain to nearly all the failed circuits:

1. Solder balls at the B+ pinouts usually showed extensive anodic corrosion; they looked dull,dark gray,compared to the normal silvery color.
2. Most substrates showed some staining or corrosive attack on the gold. This was most evident near the side edges of the substrate where moisture got in first.
3. The gold conductor to the B+ pinout may actually be corroded open if the unit is left in the test long enough.
4. The highest current resistors often opened by "burning" open at the first Au-NiCr interface from the B+ terminal.
5. The 2.5 ma resistors usually opened at the first Au-Ni-Cr interface or along the first leg of a multilegged resistor. This failure had the appearance and characteristics of electrochemical corrosion.
6. The 1.5 ma resistors usually did not open. Before that could occur, the gold conductor leading to the resistors corroded open.

7. Only resistors under power showed any failure.

Water was the major contaminant involved in corrosion problem, but other processing chemicals or epoxy residues may be accelerators. The contaminants collected at surface discontinuities and/or air pockets in the passivation materials, created during the fabrication process.

As a result of this program the following recommendations were made:

1. Check all cleaning processes to insure that cleaning is adequate and that no chemical contaminants remain.

2. Prior to final packaging, institute a 48 hour high temperature evacuation bake to eliminate volatiles and moisture.

3. Utilize hermetic packaging techniques wherever possible to provide an inert atmosphere and to prevent moisture penetration. Use fine leak test per MIL-STD-883 to insure proper package seal.

Nichrome resistors have found applications in hybrid circuits, radiation hardened circuits and as fusible links in PROM's. Reliability is important in all these applications. In hardened circuits the mission is the critical factor or perhaps one has a long term, failure free requirement because maintenance is not possible. In PROM's the sheer number of links is one additional factor and the reliability of blowing the link and having it remain open is another. SEM photographs[31], Figures 16 and 17, show a link blown by a long pulse, slow rise time. It is definitely open, Fig. 16, yet when gold is evaporated over the link, Figure 17, it becomes obvious that no meltback exists. During a short pulse, fast rise time blowing operation, it is apparent, as Figure 18 indicates, that the nichrome

SEM View of a Slow Blown Nichrome Link

FIGURE 16

SEM View of the Blown Link in Fig. 16
Overcoated with a Thin Layer of Gold

FIGURE 17

View of a Fast Blown Nichrome Link,
880X

FIGURE 18

has indeed melted and flowed. Over coating with gold in this case would reveal a canyon between link halves. Mo and Gilbert[32] have indicated that healing or relinking of slow blown fuses may be a reliability problem. Fast blown fuses have less problems but healing can still occur. The voltage to heal must be higher than the voltage used to blow the fuse. During healing one sees a small leakage current which rapidly grows under the right circumstances to provide a conducting link. Increased temperature lowers the threshold for healing. The reliability of unblown fuses follows a Weibull distribution. Lifetime for fuses can be predicted from the Arrhenius relation. Lot variability is seen and no model is available for the healing mechanism.

A military specification is available for the 512 bit bipolar PROM - MIL-M-38510/201 (USAF) 21 August 1972.

NICHROME FILMS ON OXIDIZED SILICON

Experience with nichrome was substantial by the time thin film resistors were being considered for application to integrated circuits. The advantages of nichrome were:

1. Ease of deposition.
2. Stability
3. Excellent adhesion to SiO_2.
4. Good temperature characteristics.
5. General availability.

Occasionally, complaints about process difficulty and product variability were heard, but nothing serious. In these circuits, aluminum is used as the contact metal. Intermetallic formation and Kirkendahl void formation did not seem to be a problem. The diffusivity of chromium in aluminum up to 605°C

is independent of diffusion time, thus ruling out the possibility of Kirkendahl effects[33]. This paper also indicates the diffusivity of both chromium and nickel in aluminum is extremely slow.

TABLE IV

Diffusivity and Activation Energy for Diffusion of Ni and Cr in Aluminum

D. (cm^2/sec)	$2.9X10^{-8}$	$3.0X10^{-7}$
Q (ev)	0.66 ev	0.67 ev

Of course the values for diffusivity may not hold for the very thin films.

The only real problem discussed at any length concerning nichrome resistor processing was the chemical corrosion introduced by water in J-100 photoresist stripper. Philofsky, Stickney and Ravi[34] gave some observations on the reliability of nichrome resistors having a 30% Ni-70% Cr composition. These films were evaporated onto thermally oxidized silicon and aluminum contacts were used. The films were about 150 angstroms thick and had a sheet resistivity of about 200 ohms per square. Thicker films having lower sheet resistances were easier to fabricate and were less susceptible to aging effects. Good films showed less than 1% per 1000 hours change in resistance during 300°C storage. Similarly, they showed less than 1% per 1000 hours change under 50 milliwatts per square mil power dissipation at a substrate temperature of 200°C. With low temperature glass passivation following thermal oxidation for trimming and stabilization, the resistors would withstand the heat treatment necessary to form low resistance aluminum-silicon contacts.

These investigators noted the absence of voids and porosity during

examination of the films in an electron microscope. This surprising result is probably due to the smooth thermal silicon dioxide and the lack of preferred nucleation sites. They also noted that:

1. As deposited, three phases were apparent. Two phases are in the form of fine particles and cannot be identified.

2. The films have a body centered cubic structure. From the equilibrium diagram, one would have predicted a 50% body centered cubic chromium solid solution and a 50% face centered cubic nickel solid solution.

3. Aging at 500°C for 15 minutes resulted in growth of the light colored phase, to particles of 2000 angstroms average diameter.

4. Samples having 500 angstroms of aluminum vacuum deposited on 150 angstroms of nichrome, 30Ni-70Cr composition, showed the growth of a new phase in the form of islands greater than 200 angstroms in diameter, when aged at 500°C for 15 minutes. The new phase had a complex structure.

5. No electromigration failures were observed below 4×10^{-6} amps/cm^2 at an ambient temperature of 200°C. Failures which occurred early, before 500 hours, appeared to be the result of exceeding the fusing current at nonuniformities in the films. The lowest current density for failure was 4.2×10^6 amps/cm^2. It was recorded on one of the early failures. The upper density for a good part is about 1×10^7 amp/cm^2. Fusing was the mechanism which destroyed the resistors at that level.

6. Power cycling could generate thermomechanical stresses because of thermal expansion coefficient differences between SiO_2, NiCr, and the passivating glass. No failures were observed however, after more than 7 billion cycles at the highest power level applied. Power density was more than 50 times that expected during normal operation. Current densities up to

$5.9X10^5$ amp/cm^2 were used.

7. At a power density sufficient to give an estimated chip temperature above 300°C and a current density of $5.2X10^6$ amp/cm^2, aluminum was observed to migrate onto the resistors in the form of a filament. In all cases the aluminum filaments grew from the positive terminal, in the direction of the maximum field. Reversing the polarity did not cause filament shrinkage. Instead, new filaments grew from the new positive terminal. The conditions are such that filaments probably nucleate at nonuniformities in the edge of the aluminum contact and the molten aluminum generated by the high power dissipation, grows by electrolysis in the direction of maximum field.

8. Intermetallics formed in the Ni-Cr-Al system are susceptible to preferential attack by the common etchants used to delineate aluminum. In normal processing the intermetallics would not be present at the time aluminum conductor and contact geometries are formed.

9. Inadequate process control and clean up treatments can allow trapped moisture and etching solutions. These materials can cause subsequent failure by chemical corrosion.

Barry[35] made a study of electrochemical voiding of nichrome resistors on oxidized silicon. He listed the following necessary conditions:

1. The anode must be the nichrome resistor.

2. The cathode is some adjacent metal line, or another portion of the same resistor.

3. An electrolyte within the package which will condense at some reduced temperature. Neither water by itself nor carbon-dioxide in the water is a sufficiently good electrolyte

4. Cracks or voids in the passivation glass.

5. External potential.

Coating the circuit with a second layer of passivation glass seals the cracks and reduces the susceptibility to electrocorrosion. Additional protection can be achieved by lowering the sealing temperature and keeping the quantity of sealing glass to a minimum. Barry obtained two, three point curves which give a comparison of the MTF (mean time to failure) for unpassivated nichrome at two different temperatures under applied voltage. Figure 19 gives the cumulative failures as a function of time for unpassivated resistors held at 25°C with 2 volts applied to each resistor. Figure 20 gives the same information for identical resistors operated in the same way at -25°C. The resistors at 25°C did not have a very good MTF, 48 hours, but at -25°C the MTF dropped almost two orders of magnitude to 0.55 hours. The water content in the ceramic packages was not given.

Paulson[36] has extended the work of Ravi,and Philofsky and Stickney under an RADC contract. Following is a summary of the contract.

The resistors used in this work were electron beam evaporated from a 70Ni-30Cr source to give film resistors having a 30Ni-70Cr composition. The composition was determined by microprobe analysis. For these films the TCR was found to depend on film thickness and vacuum annealing. Figure 21 displays the information. The TCR was larger for the greater thickness, and increased with vacuum annealing. Figure 22 shows how the resistance and the TCR changed during aging at 500°C in oxygen. The low, stable TCR value for these films after 30 minutes at 500°C, is very interesting and useful to anyone requiring precision resistors.

Figure 19

Cumulative Percent Failure vs. Time for Unpassivated NiCr Resistors in Ceramic Flatpacks, Operated at 25°C Ambient

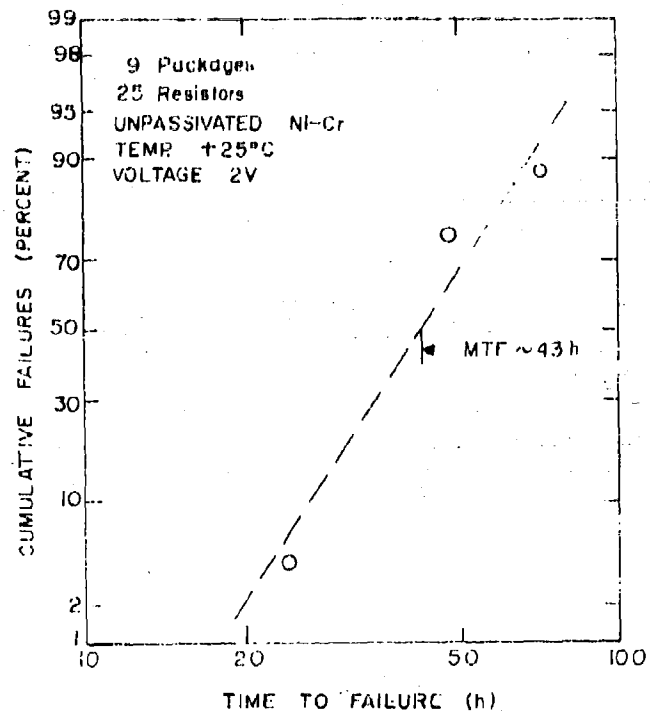


Figure 20

Cumulative Percent Failure vs. Time for Unpassivated NiCr Resistors in Ceramic Flatpacks, Operated at -25°C Ambient

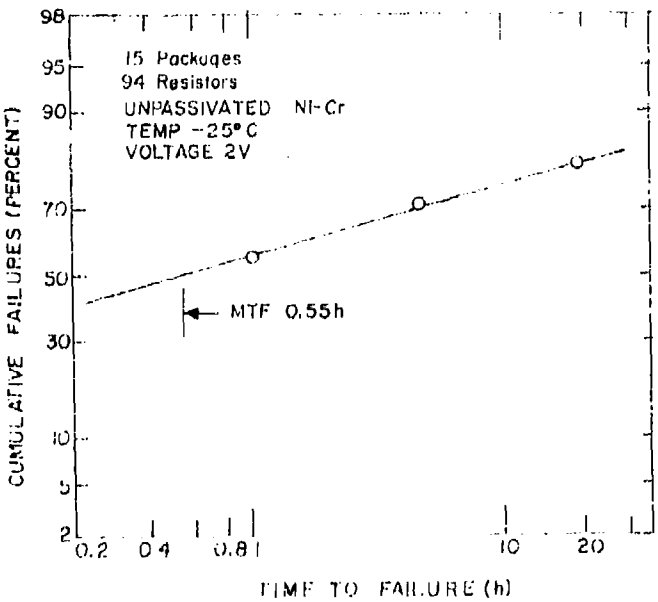
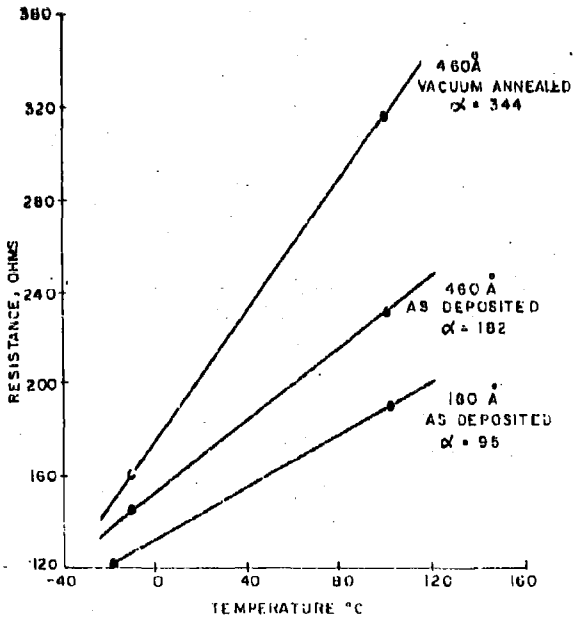
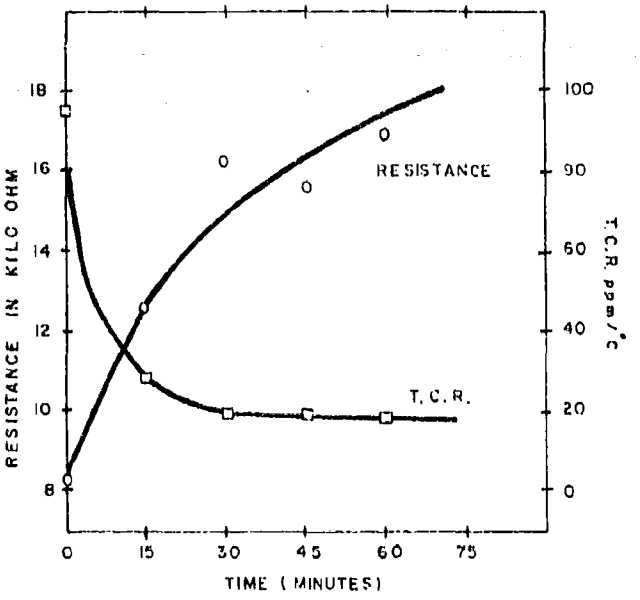


Figure 21



THE EFFECT OF THICKNESS AND ANNEALING ON THE TCR FOR Ni Cr RESISTORS

Figure 22



CHANGES IN THE RESISTANCE AND TCR CAUSED BY AGING Ni Cr RESISTORS AT 500°C IN AN OXYGEN ATMOSPHERE

Corrosion was studied in both forms, chemical and electrochemical. Pourbaix diagrams for nickel, chromium and aluminum were found which are useful in predicting corrosion behavior. They show that both nickel and chromium form stable oxides in neutral and basic solutions, but are corroded in acid solutions. Aluminum corrodes in either acidic or basic solutions. At a high enough voltage, both nickel and chromium are subject to corrosion. For chemical corrosion experiments both NiCr thin films and NiCr resistors with aluminum metallization were immersed in different solutions to determine the susceptibility to corrosion in those solutions. Table V lists the solutions and the degree of attack on the two types of samples. A 1:10 solution of HF in water will etch the glassivation and then attack the nichrome. This attack was particularly severe at the Al-NiCr interface. Probably the glass was cracked or contained voids at the step allowing easy access of the HF solution. Similarly, the attack of 5% H_2O in J-100 photoresist stripper was particularly severe at the Al-NiCr interface.

The second set of corrosion experiments involved placing water drops on the resistors and applying voltage. These tests were suggested by RADC and the procedure was worked out at RADC in support of the contract. Basically, Paulson found no corrosion at less than about 2.5 volts applied for nichrome, but aluminum will corrode down to 0.5 volts, applied. For nonpassivated resistors failure occurred by opening the resistor at the positive edge of the water drop. Metal was transported away. For oxidized resistors, failure was again an open, but this was a result of oxidizing through the remaining metal. Glassivated circuits covered with water showed attack only at the aluminum pads. Even without glassivation

TABLE V

Degree of NiCr Attack by Various Chemical Solutions

At Room Temperature Unless Stated Otherwise

Solution	NiCr	NiCr and Al
Conc. HNO_3	No Attack 1 hr.	No Attack 1 hr.
Conc. HCl	No Attack 1 hr.	No Attack 1 hr.
1-HCl 1-H_2O	No Attack	No Attack
1-HNO_3	Slowly Dissolves	Al Dissolves
1-HCl 1-H_2O	1 hr.	5 min., NiCr Slowly Dissolves
1-HF 10-H_2O	Spotty Dissolution 10 min.	Slowly Etches Al and NiCr
Solution B (H_3PO_4, HNO_3 and H_2O	No Attack	Al Dissolves 1 hr.
Solution B $Ce(SO_4)_2$ (NiCr etch	No Attack 90 min.(70°C) Dissolves 1 min.(60°C)	Al Dissolves 30 sec.(70°C) Al and NiCr Dissolve Slowly(60°C)
$(NH_3)_2Ce(NO_3)_6$ (NiCr etch)	Dissolves 1 min.	Only attacks NiCr
Aqua Regia	No attack 1 hr.	No attack 1 hr.
$FeCl_3$(1.4g/ec)	Pits NiCr	Dissolves Al
J-100	No Attack 3 hrs.(105°C)	No Attack 3 hrs.)105°C)
J-100 + 5%H_2O	No Attack	Attacks Both Al and NiCr
10% NaCl	Pits NiCr	Dissolves Al
10% K Cl	Pits NiCr	Dissolves Al

however, if the water drop touched both the aluminum and the nichrome, the aluminum would sacrificially corrode, leaving the nichrome resistors intact. This "galvanic protection"[37] is related to the relative areas of aluminum and nichrome as well as to chemical reactivity. The equations of concern in electrochemical corrosion of nichrome are as follows[38]:

$$Cr_2O_3 + 5H_2O = 2CrO_4^{=} + 10H^{+} + 6e^{-}$$

$$E = +1.386 - 0.0985pH + 0.01971\log(CrO_4^{=})$$

and

$$2\,NiO + H_2O = Ni_2O_3 + 2H^{+} + 2e^{-}$$

$$E = +1.032 - 0.059\,pH$$

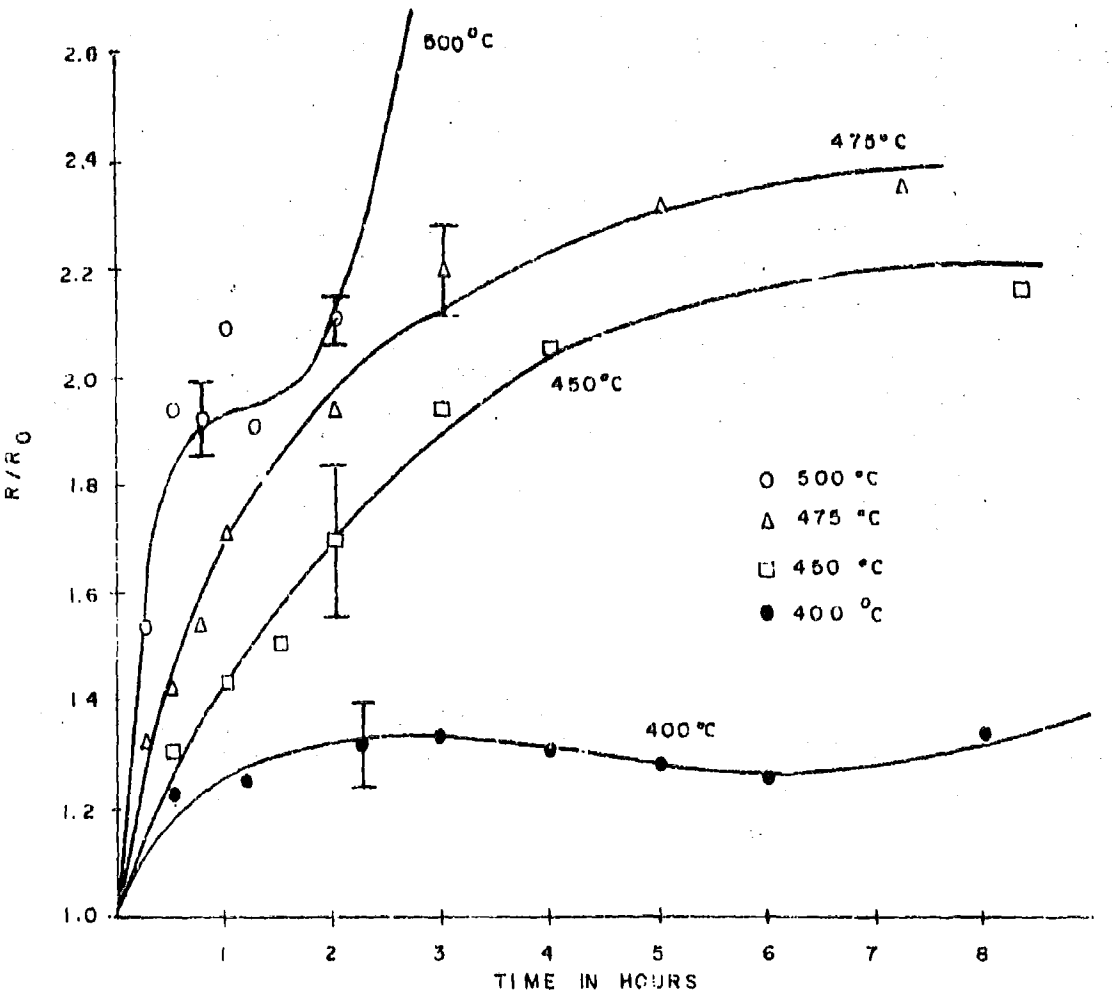
E = Electrochemical Potential in Volts

Aluminum oxide is stable at nearly all potentials in a neutral solution. At the anode, however, water decomposes and the local pH decreases. Thus the solution becomes locally acidic and corrosion ensues.

The resistance of an as deposited nichrome film will change as it is oxidized. Figure 23 shows the changes in 30 Ni-70Cr resistors as a function of time at various temperatures in oxygen. This treatment is used to stabilize and protect the resistors prior to glassivation. Different thickness films will behave differently during oxidation, although the general shape of the curve is the same. Even the shape may change for fairly thick films (800 angstroms or more).

The films seem to show nonuniform oxidation. Resistance changes are due not only to oxidation, but also to precipitation, grain growth, and in-

Figure 23



THE CHANGES IN RESISTANCE AS A FUNCTION OF TIME AT 400, 450, 475 AND 500°C IN AN OXYGEN ATMOSPHERE FOR 180 Å NiCr

terdiffusion. The oxidation behavior is indicative of a two step process. There is an initial rapid surface and grain boundary oxidation, followed by a diffusion limited oxidation process. Because there is proportionally more grain boundary area in a narrow resistor as opposed to a wide one, the rate of change in resistance for a narrow resistor is greater than that for a wide resistor.

Figure 24 shows the differences in aging characteristics for two different nichrome compositions. The high chromium composition film is the better behaved film.

Kinetics for the interdiffusion of Ni-Cr and Al were obtained by heating resistor test patterns with aluminum metallization. Aluminum diffuses into and forms intermetallic phases with nichrome. Figure 25 gives the penetration of aluminum into 30Ni-70Cr nichrome films as a function of time at 525°C. An Arrhenius plot of the diffusion data is shown in Figure 26 assuming the relationship; $D = D_0 \exp(-Q/RT)$ where $D(cm^2/sec) = 2.09 \times 10^{9}$, 1.17×10^{-10} and 1.4×10^{-11} for temperatures 525°C, 500°C, and 475°C respectively. An activation energy of 36 ± 30 kcal/mol was determined and D_0 was found to be of the order of 10^{16} cm^2/sec. The rate limiting step in the process is probably intermetallic phase formation.

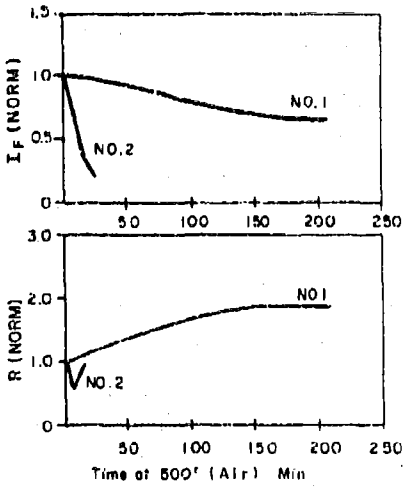
Temperature cycling tests with bias were conducted on packaged test patterns. 300 resistors were tested. The test was conducted as follows:

1. Raise temperature to 125°C and maintain for 3 hours.

2. Decrease the temperature to -55°C and maintain for 3 hrs. Power cycle the devices during this time, 2.5 minutes on, 2.5 minutes off. Transfer time between temperatures was approximately 5 minutes.

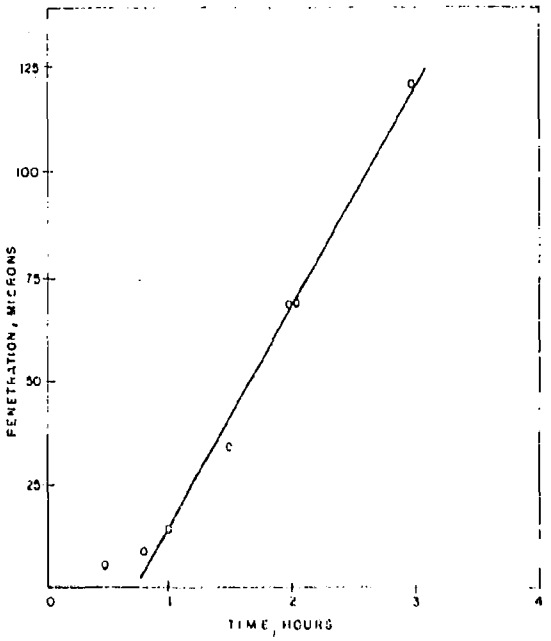
3. Allow the devices to warm up slowly to room temperature while power

Figure 24



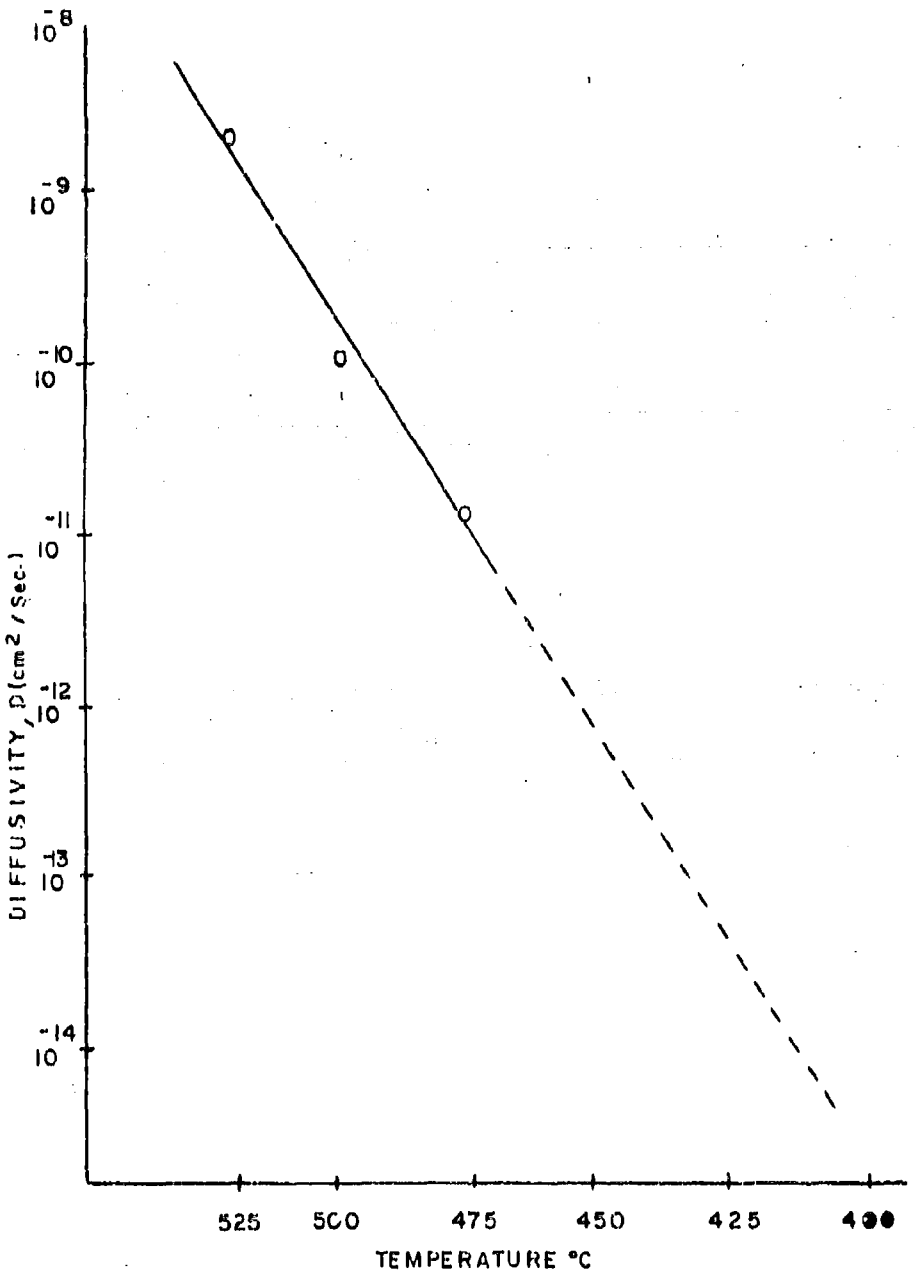
THE EFFECT OF COMPOSITION ON THE AGING OF NiCr RESISTORS. NO. 1, Ni-70Cr; NO. 2, Ni-32Cr

Figure 25



PENETRATION OF ALUMINUM INTO NICHROME AS A FUNCTION OF TIME AT 525°C

Figure 26



AN ARRHENIUS PLOT FOR THE DIFFUSION OF Al INTO NiCr

cycling at the same rate. Table VI shows resistance measurements of 12 resistors in 2 packages at different stages in the test. Resistor values changed very little after 32 cycles and no failures were encountered.

RADC supported this contract with water drop test analysis and gas ambient analysis. Those results follow.

RADC IN-HOUSE CONTRACT SUPPORT

Deionzed Water Drop Test

A water drop test was performed on a number of unglassivated film nichrome resistors deposited on an oxidized silicon substrate to determine if they could be attacked by moisture.

Drops of DI water was selectively placed on the surfaces of several thin film nichrome resistors with and without applied bias to the resistor terminals. Without applied bias there appeared to be no degradation, although there was some residue left on the surface. With applied bias, resistors shown in Figure 27 opened within one minute. The long resistor indicated by the arrow was biased at 8 volts with a load current of 1ma. The open occurred at the positive electrode. The two wavy resistors on either side of this bias resistor were also opened. It is apparent that the field, in these regions, was sufficient to cause electrochemical corrosion of these other resistors. A closeup of these resistors is shown in Figure 28.

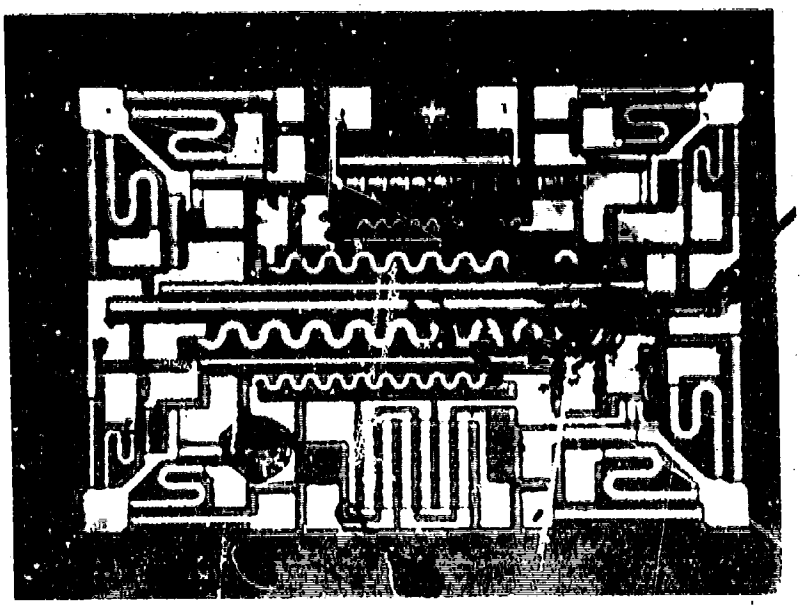
Some additional tests performed on some of these resistor patterns indicated the following:

1. If the drop of DI water totally covers the resistors and aluminum metallization pads, the aluminum pads corrode first and leave the resistor patterns intact.

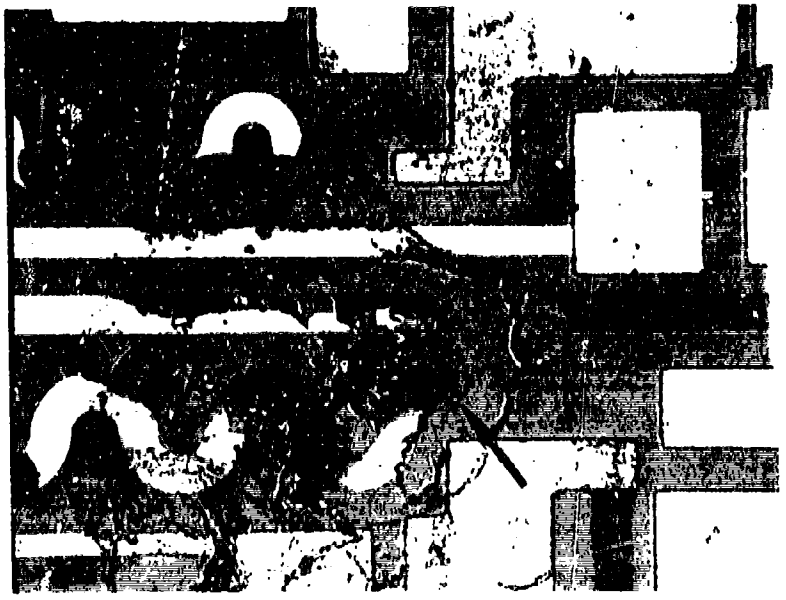
TABLE VI

Representative Values for Ni Cr Resistors that Were Temperature Cycled Between + 125°C and -65°C With a Bias Applied at the Low Temperatures

Device No.	R1	R2	R3	R4	R5	R6
#675						
Initial	66.1	1883	7751	68.0	1892	7644
1 Cycle	62.8	1877	7754	70.0	1889	7643
6 Cycles	63.3	1873	7750	71.0	1891	7639
32 Cycles	65.3	1860	7712	63.0	1875	7602
#690						
Initial	73.8	2072	8560	74.0	2076	8490
1 Cycle	70.8	2063	8560	77.0	2070	8448
6 Cycles	70.0	2065	8550	74.0	2069	8480
32 Cycles	71.8	2050	8497	67.0	2055	8425



Open NiCr Resistors After Biasing-60X
Figure 27



Open Adjacent NiCr Resistors - 240X
Figure 28

2. For the larger thin film resistor widths, a drop of DI water w/bias may not cause failure. It may only decrease the resistance. The residue remaining from the dried water drop may be conductive enough to cause the decrease in the resistance.

The narrow thin film resistors that are adjacent to a wider thin film resistor which is biased, will fail almost immediately, even though they are not directly biased.

WATER DROP TEST ON FLIP-FLOP

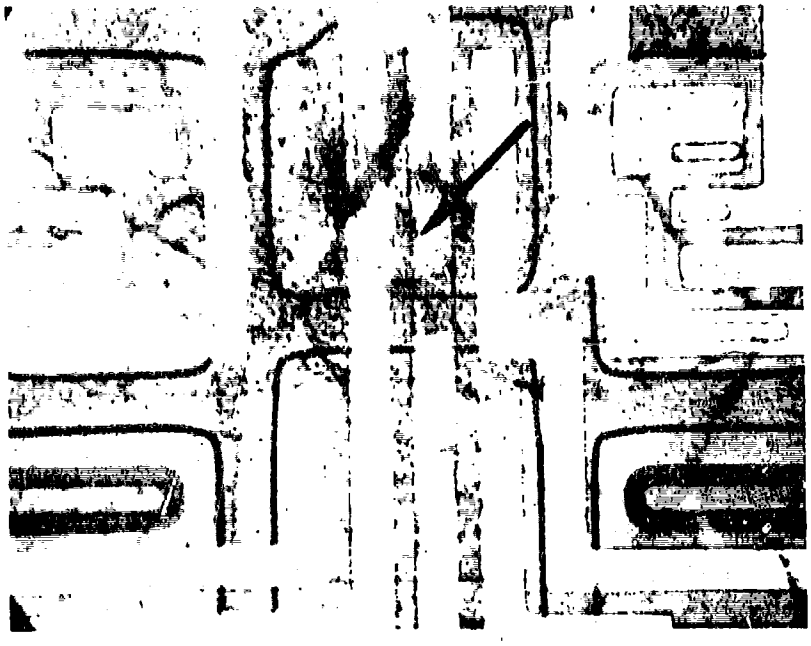
A decapped flip-flop circuit was subjected to a sequence of tests as follows:

450°C - Bake for ten minutes to simulate sealing temperature.

Five cycles water drop test - with bias but without output loading (one cycle = 3 minutes or until water evaporates.)

Two cycles of water drop test with bias and with output loading 2.0k ohms.

The circuit was biased +6.0 volts and the set "A" and set "B" side were activated to set "A" side high and then "B" side high. The circuit was baked at 450°C for 10 minutes to simulate the sealing temperature operation and to denote any effect on the glassivation over the device chip. There was no apparent crazing or cracking of the glass. The device was then subjected to the five cycles of DI water. After the fifth cycle there appeared to be some corrosion. A close examination of the chip showed that some of the aluminum metallization had disappeared. This indicated there were some pinholes in the glassivation as noted in Figure 29. No nichrome corrosion was found.



Corroded Al Metallization After 5
Cycles DI Water w/Bias-270X

Figure 29

CONCLUSIONS:

The unglassivated thin film nichrome resistors, when subjected to moisture for several minutes without bias, showed no degradation of the resistors.

The unglassivated thin film nichrome resistors when subjected to moisture with applied bias above a minimum threshold voltage of 3.0 volts will fail.

The narrow thin film nichrome resistors (0.5 mil) that are within the water drop and electric field also fail even though bias is not applied to the terminals of the resistor.

When a drop of DI water totally covers the thin film nichrome resistors and also the aluminum metallization pads under biased conditions, the aluminum pads will corrode first leaving the resistor pattern intact.

The water drop experiment performed on the flip-flop circuit using thin film nichrome resistors coated with a surface glassivation layer, indicated that the glassivation was adequate to protect the resistors.

However, after 5 cycles of DI water with bias to the circuit, there was some aluminum metallization corrosion which is indicative of pinholes in the glassivation.

RADC PACKAGE AMBIENT EXAMINATION:

Two groups of packaged test patterns were examined, those which had been through cycled temperature, on-off power tests, and those which although packaged the same day, on the same equipment, had not been placed on test. The packaging ambient contained more than 20% oxygen. Packages were sealed at 460°C with a pyroceram (PbO_3) type glass. It is known that oxygen is

taken up by the pyroceram during sealing.

At first 3 tested and 3 nontested packages were opened. The results were very surprising. Table VII gives the data. The high nitrogen content, low oxygen and 0.6% water vapor in the untested packages were quite unexpected. We thought the oxygen would be much higher and the water content lower. Even more surprising was the apparent radical change in the nitrogen and oxygen percentages in the tested packages. Since these are relative percentages, the absolute quantity of one of the gases may be constant. If the nitrogen gas volume was constant then somehow more oxygen was generated during testing. The pressures in the tested packages did seem to be higher than those in the nontested packages. In both types the internal pressures were less than one atmosphere. This indicates that the seal was made at one atmosphere pressure, at elevated temperature. Thus one would conclude that a positive pressure is maintained in the package during the sealing operation. The fact that internal oxygen is reacting with the pyroceram must be considered since this effect along could explain the reduced pressure.

The packages had been heated at 125°C for at least 48 hours prior to opening. It did not seem that the desorption of oxygen could explain the increase in oxygen content for the tested group. We therefore set up a test in which seven nontested packages were selected and split into two groups. The group of 4 was kept as a control; the group of three was subjected to -65°C for 8 hours and then temperature cycled. The schedule was:

1. 25°C to 125°C, air to air, 10 minutes
2. Hold at 125°C for 15 minutes

TABLE VII
Gas Ambient Analysis of Tested
And Nontested Packages As Received

	Nontested			Tested		
Hydrogen	4.1%	0.1%	1.1%	0.0%	0.0%	0.1%
Nitrogen	92.5	89.2	96.0	39.9	31.0	64.2
Oxygen	< 0.1	5.0	0.0	49.5	63.0	30.7
Water	0.6	< 0.1	0.6	0.4	0.0	0.1
Carbon Dioxide	2.5	5.2	1.9	9.9	5.5	4.6
Argon	0.2	0.5	0.4	0.2	0.4	0.2
Methane	0.1	< 0.1	< 0.1	0.1	0.1	0.1
Torr	.0082	.0063	.0094	.0098	.0098	.0082

TABLE VIII
Gas Ambient Analysis of Tested And
Nontested Packages After Temperature Cycling

	Noncycled Nontested				Temp. Cycled Nontested		
Hydrogen	0.0%	3.7%	1.5%	1.8%	*0.0%	0.0%	0.7%
Nitrogen	99.2	92.1	94.2	96.6	74.4	92.2	97.7
Oxygen	0.0	0.0	0.0	0.0	15.9	3.8	0.0
Water	0.0	0.0	0.0	0.0	1.4	0.9	0.0
Carbon Dioxide	0.5	4.0	4.2	1.3	8.1	1.6	1.4
Argon	0.3	0.2	0.1	0.3	0.1	1.5	0.2
Methane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Torr	.0048	.0057	.0058	.0099	.0154	.0413	.0100

3. 125°C to 25°C, air to air, 10 minutes
4. Hold 25°C for 15 minutes
5. 25°C to -65°C, air to air, 10 minutes
6. Hold at -65°C for 15 minutes
7. -65°C to 25°C, air to air, 10 minutes

Twenty five cycles were executed and then all seven packages were placed in the mass spectrometer - package opener assembly. They were held at 125°C for 48 hours and then opened. The results are given in Table VIII. Essentially these results do not differ from the first group of untested packages with the exception of one package which looks suspiciously like a leaker. Its data is starred.

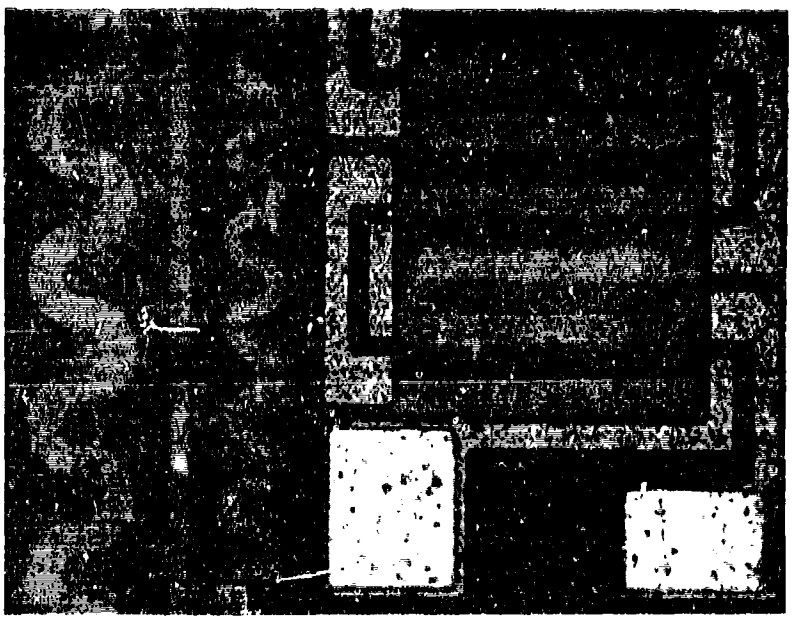
Since neither temperature extremes nor temperature cycling produces any additional oxygen, one must conclude that either some reaction is occurring as a result of operation under power, which generates oxygen, or there are variations from zero to 63% in the initial oxygen content, and we just happened to pick sets of packages which showed very different groupings. This is possible because the tested group was probably run at one time and the nontested at another time the same day. Two packages gas analyzed at Motorola did not show the large variation between tested and nontested. The data from both packages looked like the results we obtained for nontested packages. Table IX gives the composite results thus far. More packages must be examined to settle the question. In any case, we do know that large variations in gas ambients exist within these sealed packages, and moisture content as high as 1.4% of the total gas volume is possible. We also know that gas ambients can interact with materials within a sealed

TABLE IX
Summary of Gas Ambient Analysis of Tested
And Nontested Nichrome Test Pattern Packages

	Nontested (10) AVE %	Max. Var.	Tested (3) AVE %	Max. Var.	Significant Change AVE %	Max. & Min.
Hydrogen	1.0	+3.1 -1.0	0.1	±0.1		
Nitrogen	92.4	+6.8 -18.0	45.0	±14.0	47.4	68.2 15.4
Oxygen	2.5	+13.4 -2.5	47.7	±17.0	45.2	64.7 14.8
Water Vapor	0.35	+1.05 -0.35	0.2	±0.2		
Carbon Dioxide	3.1	+5.0 -2.6	6.3	±3.6		
Argon	0.38	+1.1 -0.28	0.3	±0.1		
Methane	0		0.1	±0.1		

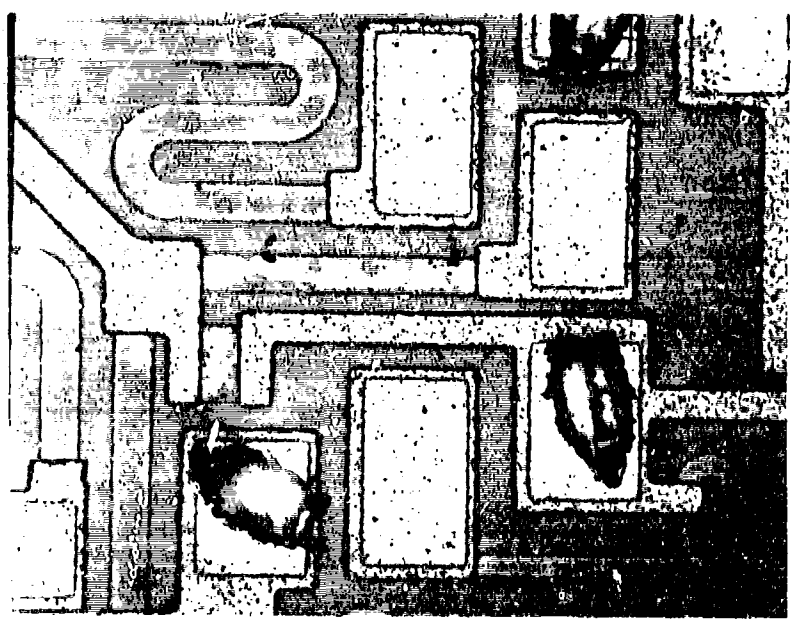
container. For example, metal oxides may give up oxygen to maintain the following equilibrium, $CO_2 \rightleftharpoons CO + 1/2\ O_2$ under the equilibrium conditions $P_{O2} = K^2_D\left[\frac{P_{CO2}}{P_{CO}}\right]^2$ Similarly, the equilibrium $2H_2O \rightleftharpoons 2H_2 + O_2$ must be maintained according to $P_{O2} = K_D\left[\frac{P_{H2O}}{P_{H2}}\right]^2$ Actually, these two equilibrium conditions are coupled because $H_2 + CO_2 \rightleftharpoons CO + H_2O$.

Following gas ambient analysis, the test chips were inspected visually. It was immediately noted that color variations were often seen in the glassivation. The variations were not correlated with tested or untested packages. Even the presence of large color variations over nichrome resistors was not correlated with resistor value variation. Figure 30 shows a portion of a test chip where no color variation was seen. Figure 31 shows a portion of a test chip where significant color variations were seen. At this point we have no reason to suspect any reliability problem. One chip shown in Figure 32 had rather sharp color variations over the nichrome, next to the aluminum terminations. From past experience with nichrome, there would be a strong desire to reject this type of color variation as a possible reliability hazard. Yet this chip survived the 32 temperature cycle test with cycled power described earlier. At first glance, one might expect a loss of glass adherence or a much different glass film thickness over the discolored region. SEM analysis did not indicate any adherence problem and, as Figure 33 shows, it did not reveal any structure correlation with the discolored region. An interesting dip in glass thickness at the nichrome-aluminum contact was noted however, and is shown in Figure 34. Again more samples are required to evaluate the incidence of these effects and their cause or causes.



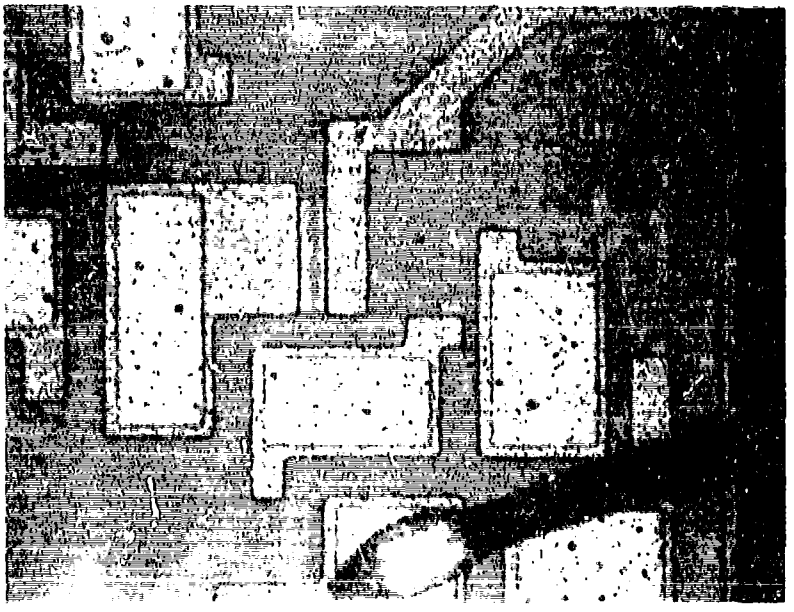
Portion of Glassivated Nichrome Test Pattern; No Color Variations Over the Nichrome

FIGURE 30



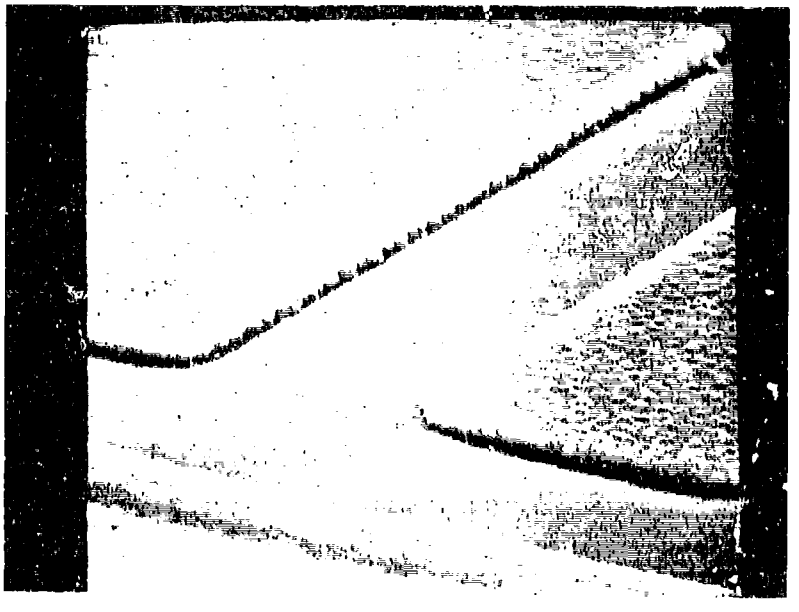
Portion of Glassivated Nichrome Test Pattern with Pronounced Color Variations Over the Nichrome

FIGURE 31



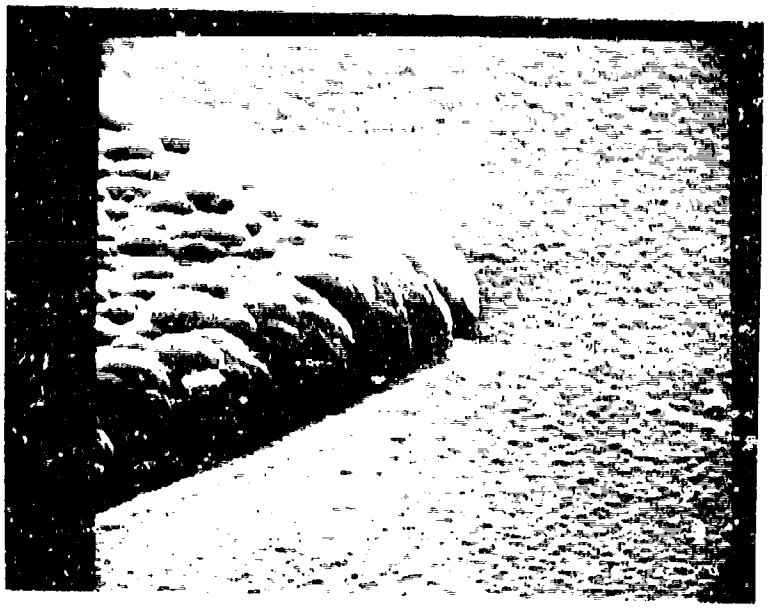
Portion of a Glassivated Nichrome Test Pattern Showing Color Variations Over the Nichrome at the Aluminum Contacts

FIGURE 32



SEM View of the Short, Wide Nichrome Resistor in Fig. 32 No Structural Correspondence with the Color Variation

FIGURE 33



SEM View of Glassivation Over the Aluminum to Nichrome Contract Shown in Fig. 33

FIGURE 34

CONCLUSIONS AND RECOMMENDATIONS:

During this study, it was clear that corrosion was the most important concern, in particular, electrochemical corrosion. Nichrome films do not suffer from electromigration or Kirkendahl voiding due to interaction with aluminum. Their very thinness however, makes them vulnerable to overstress and corrosion. For this reason processing and packaging are extremely important. Small amounts of contaminants, a few picograms in the right place, are sufficient to destroy a resistor. Presently, good process control and appropriate screens prevent and remove problems. Still there is the ever present concern over long term problems not picked up by the screens. In our opinion this study and related experience with nichrome resistors suggests the following recommendations:

1. A better screen and accelerated moisture test is needed.

2. Passivation glasses and glass deposition techniques need further study.

3. Packages, packaging materials and procedures, and the effects of internal package ambients need to be studied. Packaging ambients themselves should be standardized and controlled. Our goal should be to keep the moisture content in I.C. packages to less than 5 ppm. The dew point at -65°C is about 5.3 ppm.

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